

# Analyzing Line Emission Spectra viewed through a Spectroscope using a Smartphone

Eugene T. Smith, PhD

## Goals:

1. Calibrate spectroscope using mercury emission source or fluorescent bulb.
2. Determine wavelengths of hydrogen emission.
3. Calculate the value of the Rydberg constant.
4. Observe emission lines of various salts.

## Introduction

In the first periodic tables, elements were arranged by chemical properties/reactivity with no understanding of why some elements had similar properties. Our modern day periodic table is now organized based on electronic structure, and our understanding of chemical properties and periodic trends is more complete. Electronic structure is important in our understanding of chemistry, and the following exercise serves to illustrate how the organization of electrons in an element was originally deduced.

Individual atoms are too small to see with the naked eye so indirect methods are employed to obtain structural information. The interaction of atoms with light is one of the most useful tools in determining atomic structure. Both atoms and molecules absorb and emit light at characteristic wavelengths due to transition of electrons between different energy states.

The wavelength of emission lines is related to the difference in energy between electronic states according to the following expression:

$$\lambda = \Delta E_{\text{transition}} / hc, \quad (1)$$

where  $h$  and  $c$  are the Planck's constant ( $6.626 \times 10^{-34}$  J·s) and speed of light ( $3 \times 10^8$  m/s), respectively. In this application, electrical energy is used to excite gaseous

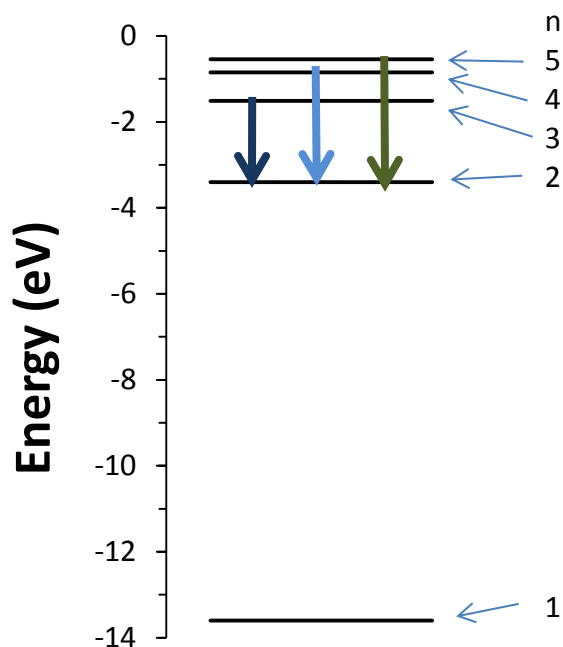


Figure 1. Energy diagram illustrating electronic transitions of hydrogen observed in the visible spectrum.

atoms to higher energy states, and the light, at discrete wavelengths, is observed as high energy electrons return to the ground state. Energy diagrams, as illustrated in the Figure 1, are commonly used to illustrate different electronic states (solid lines) and energy transitions (arrows).

As discussed in lecture, elements, such as hydrogen, produce specific line spectra associated with discrete changes in energy levels. In contrast, when light from a blackbody radiation source, such as the sun, interacts upon a diffraction grating, a continuous spectrum, or rainbow, will be observed. Hydrogen, since it contains a single electron, produces line spectra that can be explained using the Bohr Model. While this model can't be used to explain multi-electron systems, it still useful in providing insight into electronic structure. We will consider this relatively simple model first.

Bohr postulated that the energy of an electron in an orbit about the nucleus has an energy described by:

$$E = R_h/n^2 , \quad (2),$$

where  $R_h$  and  $n$  is the Rydberg constant ( $-13.6$  eV) and principal quantum number, respectively. Thus, it is derived that the wavelength of emitted light is:

$$\lambda = -(R_h / hc) [(1/n_f^2) - (1/n_i^2)] \quad (3).$$

In this exercise, you will calibrate a spectroscope and observe the emission lines of hydrogen. Based on your observations, you will determine what transitions (e.g.  $n = 6 \rightarrow 2$ ) are associated with each emission line, as well as the value of the Rydberg constant. Recall from lecture, visible emission lines correspond to  $n \rightarrow 2$  transitions as illustrated in Figure 1.

Unfortunately, the Bohr model described above only works for one electron (e.g. hydrogen). The field of quantum mechanics is used to describe the energy states of electrons in multi-electron systems. In this model, energy states of an electron are defined by a set of quantum numbers ( $n$ - principal,  $\ell$  -shape (angular momentum),  $m_\ell$  - orientation, and  $s$ - spin). For hydrogen, a single electron system, the energy states within a given energy level,  $n$ , are the same. However, when the number of electrons increases, the energy states within a given energy level depend on angular momentum ( $\ell$ ) due to the fact that electrons are interacting with each other.

## Sodium emission

The spectrum of hydrogen is relatively easy to interpret since its energy states only depend on the values of the principal quantum numbers, ( $n$ ). An electron in hydrogen excited to a higher energy state ( $n > 2$ ) can have energy states with different angular momentum ( $\ell$ ); however, the energy of these excited states is essentially the same. In other words, the energy is the same for an electron in hydrogen excited to a 3s, 3p or 3d orbital. In contrast, the energy of excited states for atoms containing multiple electrons depends upon angular momentum ( $\ell$ ) since electrons are shielded from the nucleus by other electrons. Thus, for all elements other than hydrogen, the energy of orbitals within a given subshell is different.

Sodium, for example, contains one valence electron like hydrogen, but this valence electron is shielded from the nucleus by ten core electrons. Due to interactions with core electrons, the energy state of excited orbitals (e.g. 3s, 3p, 3d) are different. The partial energy diagram for some excited states in sodium is shown in Figure 2.

In theory, there are a large number of excited energy states available to atoms that contain more than one valence electron. Experimentally, however, only a few transitions dominate, and these are experimentally observed as strong emission lines. “Selection Rules” are used to predict a favored or “allowed” transition, and two rules are listed in the adjacent Table.

At this point, there are probably more questions being raised than answered. Why are four lines seen for hydrogen (Figure 1), and only one for sodium (Figure 2)? What is angular momentum? Selection rules? Yes, it is complicated, so let’s back up a minute. Scientists try to rationalize experimental observations using theories. Quantum theory explains line emission spectra. As you will observe with sodium, there is a broad characteristic yellow emission line observed at approximately 690 nm. Quantum theory is used to explain why this particular emission line is observed-- it is due to an electronic transition of an excited valence electron in sodium, specifically a 3p  $\rightarrow$  3s transition. It also can be used to explain the change in energy (~2 eV), and why other transitions are not observed (selection rules).

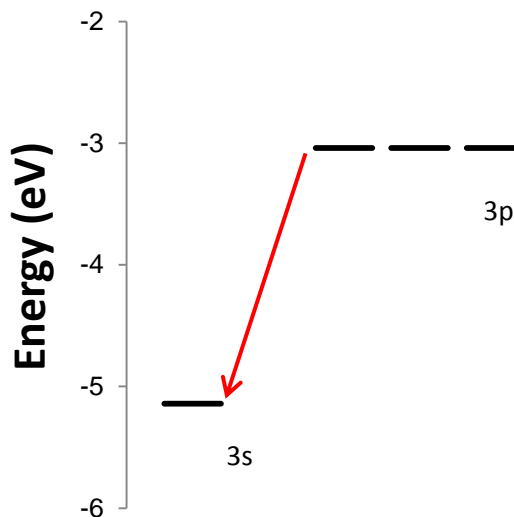


Figure 2. Partial energy diagram for sodium illustrating transitions observed in the visible spectrum.

Selection Rules	
n- principal	$\Delta n \geq 0$
$\ell$ - orbital	$\Delta \ell = \pm 1$

## Elements containing multiple valence electrons

In this lab, a spectroscope is calibrated using emission lines of mercury (either from an emission tube or fluorescent bulb that contains mercury vapor). A partial energy diagram for mercury is illustrated in Figure 3. While both mercury and sodium have core electrons, mercury has additional valence electrons that interact with each other. In addition, an excited electron in mercury can exist in different spin states. Thus, the energy states of an orbital vary within a subshell as illustrated in Figure 3.

Note in this figure that there are four different energy levels depicted for a p-orbital. You learned in lecture, however, that there are only three p-orbitals within a subshell. How is this possible? An excited electron in mercury can exist in different spin states, with each spin state having three p-orbitals available to it. One of the observed transitions ( $6d \rightarrow 6p$ ) is associated with a different spin-state of mercury.

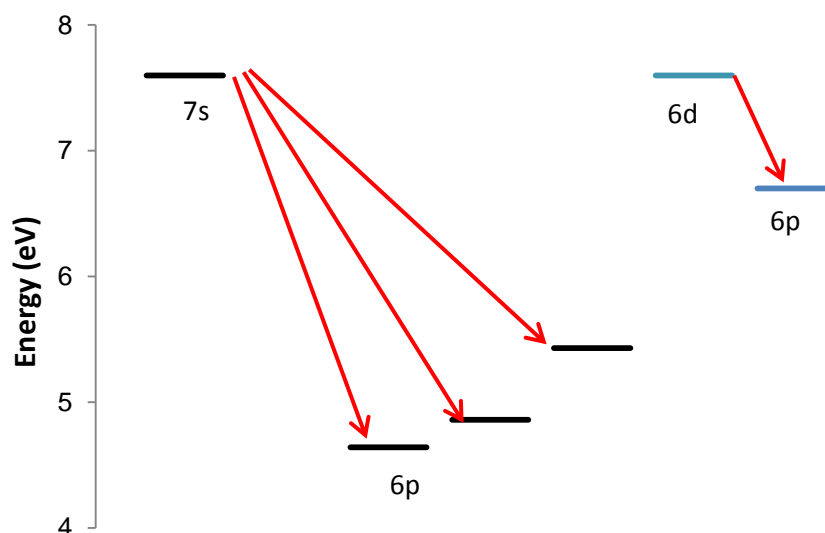


Figure 3. Partial energy diagram for mercury illustrating emission lines observed in the visible region of the spectrum.

## Procedure:

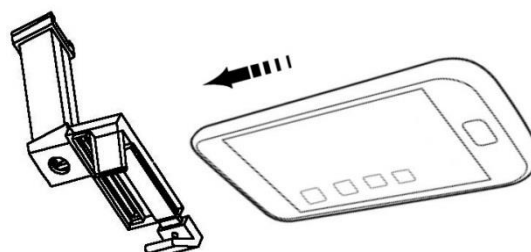
A spectroscope can be used to observe electronic transitions. A diffraction grating is used to separate light into its component wavelengths. The spectroscope is composed of a slit (a), diffraction grating/telescope (b), and scale (c). The slit produces parallel or collimated light, which is then separated into component wavelengths by the diffraction grating. The scale will be generated by your smartphone by calibrating it against known emission lines. Once your scope is calibrated using a mercury emission source, you can determine wavelengths of hydrogen emission, and calculate the value of the Rydberg constant. Lastly, you will observe the emission line of sodium.

### Calibration of scope

To measure the wavelengths of hydrogen, we need to use a calibrated spectroscope. This will be done by calibrating the scope with emission spectra of mercury or a fluorescent light. See instructions below.

#### Part A. View a continuous light source.

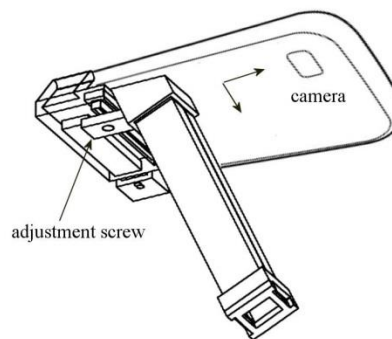
1. Attach the spectroscope to a smartphone by sliding the phone through the adjustable clips.
2. Align phone camera with scope.
3. Expose the spectroscope as at a continuous light source, such as an incandescent bulb or the sun (Be careful not to stare into the sun!).



Step 1. Attach scope to smartphone

Do not point the spectroscope at the sun or the image will appear overexposed. Good results can be obtained with the sun behind you.

Adjust the angle so that only a single rainbow appears. You may have to shield the space between the phone and scope with your hand to block out stray light.



Step 2. Align camera to scope view port

4. Adjust the slit and zoom so that the image of the rainbow appears approximately between 400 and 700 nm. The slit is adjusted manually, and the zoom buttons on the app

change the size of the image.

**Part B. Calibration using a smartphone application.**

1. View either a mercury emission tube or fluorescent source to calibrate the scope.
2. Toggle to the appropriate reference spectrum in the app, and adjust the zoom and slit until the camera image and reference image are aligned.
3. Toggle back to the scale. Your scope is now calibrated!

**Part C. Record wavelength data for hydrogen emission source.**

1. View a hydrogen emission tube through your calibrated spectroscope.
2. To determine the wavelength of an emission line, simply touch the screen, align the cursor with the emission line, and record the value.
3. To save an image of your spectrum, press the Capture Image button. The file will be stored on the external SD card on Android phones. Use the file manager and find the folder labelled Pictures (the images are not stored in the Gallery).
4. Enter data in appropriately marked spaces in Excel. Vary the values of  $n$  from the pull down menu to obtain a constant value for the Rydberg constant.

**Part E. Observing sodium source.**

1. Follow instructions and use appropriate safety precautions.
  - a. Place approximately a gram of sodium chloride on an evaporating dish.
  - b. Add approximately 0.5 mL of methanol on the sodium chloride.
  - c. Ignite the methanol with a match.
2. Observe sodium emission line using spectroscope. Do not place scope too close to flame.
3. Record emission wavelength and capture image.

Name: \_\_\_\_\_

### Hydrogen Line Emission Spectra

1. Fill in the following table. Use the Excel template provided by your instructor to determine the transition responsible for the spectral line.

Spectral line (nm)	Color	Transition

2. Using the Excel template provided by your instructor, determine the value of the Ryberg constant from your experimental data.

$R_h =$

### Mercury Line Emission Spectra

1. Mercury contains multiple electrons. The line emission spectra is influenced by the interactions of multiple electrons. Determine if the following transition is allowed (hint: use selection rules in the table of this handout).

Transition	$\Delta n$	$\Delta \ell$	Allowed	Reason for forbidden transition
4s $\rightarrow$ 3s	1	0	no	$\Delta \ell = 0$ , selection rule requires $\Delta \ell = 1$
3p $\rightarrow$ 3s				
3d $\rightarrow$ 3p				
4p $\rightarrow$ 3p				

### Sodium Line Emission Spectra

2. Sodium contains one valence electron. Fill in the following table based on your experimental observations:

Spectral line (nm)	Color	Transition



## Calculations

1. Determine the change in energy, in units of eV, required to bring about an electronic transition in the visible region of the spectrum (350-750 nm) using the equations and values in the adjacent table. Show your dimensions.

$$\begin{aligned} E &= hc/\lambda \\ 1 \text{ J} &= 1 \text{ kg} \cdot (\text{m/s})^2 \\ h &= 6.626 \times 10^{-34} \text{ m}^2\text{kg/s} \\ c &= 3 \times 10^8 \text{ m/s} \\ 1 \text{ eV} &= 1.6 \times 10^{-19} \text{ J} \end{aligned}$$

a. 350 nm

b. 750 nm

2. The emission line at 589 nm observed for sodium is due to two  $3p \rightarrow 3s$  transitions, referred to as a doublet. The difference in energy between these transitions is 0.0021 eV. Most inexpensive spectroscopes have a resolution of 5 nm. Show through calculations, that a much higher resolution spectroscope would be needed to observe the two emission lines of sodium.

a. Strategy:

$$\text{Since: } E = \frac{hc}{\lambda} \quad \text{then: } \Delta E = \frac{hc}{\Delta\lambda} \quad \text{or} \quad \Delta E = hc \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)$$

$$\text{Given: } \Delta E = 0.0021 \text{ eV} \quad \text{and} \quad \lambda_1 = 589 \text{ nm}$$

$$\text{Unknown: } \lambda_2$$

b. Make sure you are working in the correct units. Convert  $hc$  into units of  $eV \text{ nm}$

c. Substitute the value obtained in step *b* into the equation from step *a*, and solve for the second wavelength.

d. Based on your result from step *c*, does it make sense that you only observe a single emission line for sodium through your spectroscope?

Name: ANSWER KEY

### Hydrogen Line Emission Spectra

1. Fill in the following table. Use the Excel template provided by your instructor to determine the transition responsible for the spectral line.

Spectral line (nm)	Color	Transition
404.7	<i>Violet</i>	6 → 2
435.8	<i>Blue</i>	5 → 2
546.1	<i>Green</i>	4 → 2
579.0	<i>Yellow</i>	3 → 2

2. Using the Excel template provided by your instructor, determine the value of the Ryberg constant.

$$R_h = 2.18 \times 10^{-18}$$

### Sodium Line Emission Spectra

1. Fill in the following table

Spectral line (nm)	Color	Transition
<i>589 nm</i>	<i>yellow</i>	$3p \rightarrow 3s$

2. Determine if the following transition is allowed (hint: use selection rules in the table of this handout)

Transition	$\Delta n$	$\Delta \ell$	Allowed	Reason for forbidden transition
$4s \rightarrow 3s$	1	0	no	$\Delta \ell = 0$ , selection rule requires $\Delta \ell = 1$
$3p \rightarrow 3s$	<i>0</i>	<i>1</i>	<i>yes</i>	
$3d \rightarrow 3p$	<i>0</i>	<i>1</i>	<i>yes</i>	
$4p \rightarrow 3p$	<i>1</i>	<i>0</i>	<i>no</i>	$\Delta \ell = 0$ , selection rule requires $\Delta \ell = 1$

## Calculations

1. Determine the change in energy, in units of eV, required to bring about an electronic transition in the visible region of the spectrum (350-750 nm) using the equations and values in the adjacent table. Show your dimensions.

$$\begin{aligned} E &= hc/\lambda \\ 1 \text{ J} &= 1 \text{ kg} \cdot (\text{m/s})^2 \\ h &= 6.626 \times 10^{-34} \text{ m}^2\text{kg/s} \\ c &= 3 \times 10^8 \text{ m/s} \\ 1 \text{ eV} &= 1.6 \times 10^{-19} \text{ J} \end{aligned}$$

- a. 350 nm

$$E = \frac{\left(6.626 \times 10^{-34} \frac{\text{m}^2\text{kg}}{\text{s}}\right) \left(3 \times 10^8 \frac{\text{m}}{\text{s}}\right)}{350 \text{ nm} \left(\frac{1 \text{ m}}{1 \times 10^9 \text{ nm}}\right)} \left(\frac{1 \text{ J}}{1 \text{ kg} \left(\frac{\text{m}}{\text{s}}\right)^2}\right) \left(\frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}}\right)$$

$$E = 3.55 \text{ eV}$$

- b. 750 nm

$$E = \frac{\left(6.626 \times 10^{-34} \frac{\text{m}^2\text{kg}}{\text{s}}\right) \left(3 \times 10^8 \frac{\text{m}}{\text{s}}\right)}{750 \text{ nm} \left(\frac{1 \text{ m}}{1 \times 10^9 \text{ nm}}\right)} \left(\frac{1 \text{ J}}{1 \text{ kg} \left(\frac{\text{m}}{\text{s}}\right)^2}\right) \left(\frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}}\right)$$

$$E = 1.66 \text{ eV}$$

2. The emission line at 589 nm observed for sodium is due to two 3p→3s transitions, referred to as a doublet. The difference in energy between these transitions is 0.0021 eV. Most inexpensive spectroscopes have a resolution of 5nm. Show through calculations, that a much higher resolution spectroscope would be needed to observe the two emission lines of sodium.
- a. Strategy:

$$\text{Since: } E = \frac{hc}{\lambda} \quad \text{then: } \Delta E = \frac{hc}{\Delta\lambda} \quad \text{or} \quad \Delta E = hc \left( \frac{1}{\lambda_1} - \frac{1}{\lambda_2} \right)$$

$$\text{Given: } \Delta E = 0.0021 \text{ eV} \quad \text{and} \quad \lambda_1 = 589 \text{ nm}$$

$$\text{Unknown: } \lambda_2$$

- b. Make sure you are working in the correct units. Convert  $hc$  into units of  $eV \text{ nm}$

$$hc = \left( 6.626 \times 10^{-34} \frac{\text{m}^2 \text{kg}}{\text{s}} \right) \left( 3 \times 10^8 \frac{\text{m}}{\text{s}} \right) \left( 1 \frac{\text{J}}{\text{kg} \left( \frac{\text{m}}{\text{s}} \right)^2} \right)$$

$$hc = 1.99 \times 10^{-25} \text{ Jm}$$

$$hc = 1.99 \times 10^{-25} \text{ Jm} \left( \frac{1 \text{ eV}}{1.6 \times 10^{-19} \text{ J}} \right) \left( \frac{1 \times 10^9 \text{ nm}}{1 \text{ m}} \right)$$

$$hc = 1242 \text{ eV nm}$$

- c. Substitute the value obtained in step *b* into the equation from step *a* and solve for the second wavelength.

$$\Delta E = 0.0021 \text{ eV} = 1242 \text{ eV nm} \left( \frac{1}{589 \text{ nm}} - \frac{1}{\lambda_2} \right)$$

$$1.69 \times 10^{-6} \text{ nm}^{-1} = \frac{1}{589 \text{ nm}} - \frac{1}{\lambda_2}$$

$$\lambda_2 = 589.6 \text{ nm}$$

- d. Based on your result from step *c*, does it make sense that you only observe a single emission line for sodium through your spectroscope?

*Yes, the resolution of the scope is 5 nm, but the difference between the lines is 0.6 nm.*