

Experiment 17

Emission and Absorption Spectroscopy

Pre-Lab Assignment

Before coming to lab:

- Read the lab thoroughly.
- Answer the pre-lab questions that appear at the end of this lab exercise.

Purpose

A handmade spectroscope will be calibrated by measuring the emission spectrum of mercury gas then used to measure the emission spectra of a variety of cations through a flame test and hydrogen and helium gas. Rydberg's constant will be experimentally determined. The absorption spectra of CuSO_4 , CoCl_2 , and KMnO_4 will be measured.

Background

Light (electromagnetic radiation) is transmitted through space as two perpendicular waves, where one direction is electricity and the other is magnetism. In a vacuum, all light travels at the same speed ($c = 3.00 \times 10^8 \text{ m/s}$) but varies in wavelength (λ , meters), the distance between two wave crests, and frequency (ν , 1/s or Hertz), the number of waves that pass through a stationary point in one second. For any given type of light, the product of its wavelength times its frequency will equal its speed, as in Eqn. 1

$$c (3.00 \times 10^8 \text{ m/s}) = \lambda (\text{m}) \times \nu (1/\text{s}) \quad \text{Eqn. 1}$$

Light can be classified into different categories based on its wavelength/frequency. This is called the electromagnetic spectrum (Fig. 1). The visible light spectrum, or the range of wavelengths that the human eye can see, averages between 400-700 nm. Each different color distinguished by the human eye is due to a difference in wavelength.

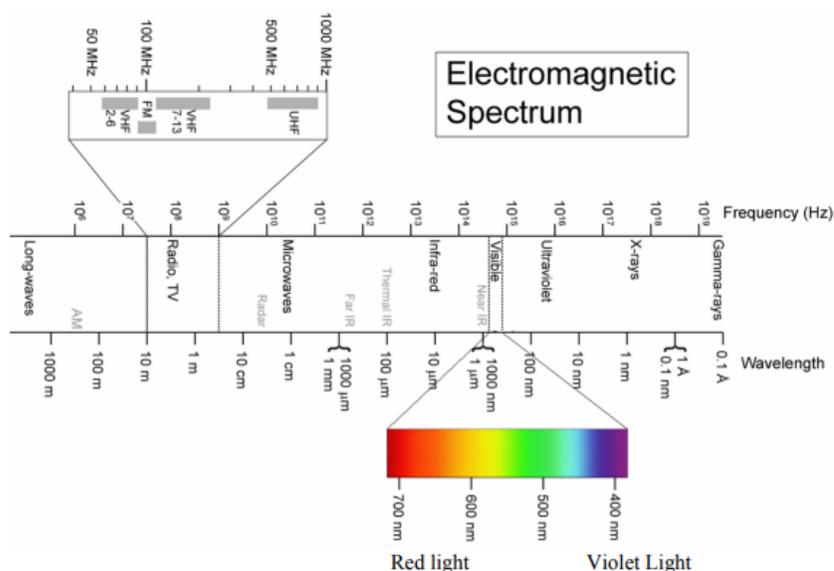


Figure 1: Electromagnetic spectrum

At the turn to the twentieth century, a number of scientists including Albert Einstein, J.J. Thompson, Max Planck, and Niels Bohr postulated that light was actually both a wave (transfer of energy) and a particle (has matter), called wave-particle duality. Light traveled as a wave of tiny, quantized packets called photons. The energy of a single photon is directly proportional to its frequency by Planck's constant (h , 6.626×10^{-34} J·s) as seen in Eqn. 2.

$$E \text{ (J)} = h \text{ (J}\cdot\text{s)} \times \nu \text{ (1/s)} \quad \text{Eqn. 2}$$

When combined, Eqn. 1 and 2 become Eqn. 3.

$$E = \frac{hc}{\lambda} \quad \text{Eqn. 3}$$

Niels Bohr postulated that electrons also exhibited wave-particle duality similar to light. As such, electrons in atoms were also confined to quantized shells that ring the nucleus, defined by the principle quantum number, n in what is called the Bohr Model of the atom. (Fig. 2). Electrons could exist on, but not between, the shells. The closer the shell is to the nucleus, the lower in energy.

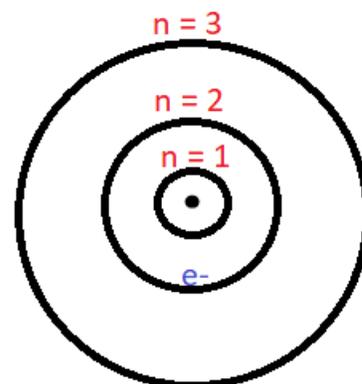


Figure 2: The Bohr Model of the atom

Electrons that absorb energy can “jump” from lower to higher shells. This process is called **excitation** and is the cause of an atom's **absorption spectrum**, or a set of wavelengths that appear as dark lines or bands. An object's visible color is the *complement* of the wavelengths absorbed; for example, an object that absorbs orange wavelengths appears visibly blue as blue and orange are complements. Similarly, electrons that release energy can jump from higher to lower shells in a process called **relaxation** that causes an **emission spectrum**, where a specific set of lines are visible. The wavelengths either absorbed or emitted are proportional to the energy absorbed or released, respectively (Fig. 3). Since the energy shells are unique to a substance, so is its absorption and emission spectra. These can be seen either by heating gaseous elements with electricity or by using metal ions as salts in flame.

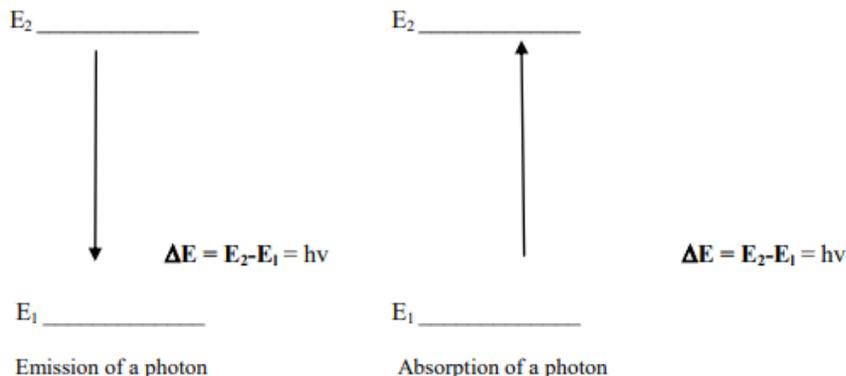


Figure 3: Relaxation of an electron by emission of a photon; excitation of an electron by absorption of a photon

Before the phenomenon of an atom's emission spectrum was properly explained, Johannes Rydberg developed a purely empirical (from experimental data, not theory) equation to calculate the lines seen for the hydrogen atom, seen in Eqn. 4.

$$\frac{1}{\lambda} = -R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad \text{Eqn. 4}$$

Here, R_H is Rydberg's constant ($1.097 \times 10^7 \text{ m}^{-1}$), n_1 is the final shell the electron moves to and n_2 is the initial shell from which the electron moved, both whole number integers ≥ 1 . If the wavelength value is negative, then it and its corresponding energy is being absorbed. If the wavelength is positive, then it and its corresponding energy is being emitted. For hydrogen, the series of emissions that fall within the visible light spectrum are called the Balmer series, where $n_1 = 2$ and $n_2 = 3, 4, 5,$ and 6 . Rydberg's constant can be determined graphically by rearranging Eqn. 4 into a linear form ($y = mx + b$) and plotting $1/n_2^2$ versus $1/\lambda$, as seen in Eqn. 5. The slope of the line will be equal to R_H and the intercept to R_H/n_1^2 when $n_1 = 2$.

$$\frac{1}{\lambda} = R_H \frac{1}{n_2^2} - \frac{R_H}{n_1^2} \quad \text{Eqn. 5}$$

$$y = m \quad x \quad + \quad b$$

Example Problem: Using Rydberg's Equation

An electron moves from the $n = 5$ to the $n = 1$ shells. Calculate the wavelength emitted, in nm. Is this transition visible to the human eye?

Step 1: Use Eqn. 5 to solve for $1/\lambda$.

$$\frac{1}{\lambda} = (1.097 \times 10^7 \text{ m}^{-1}) \left(\frac{1}{1^2} - \frac{1}{5^2} \right)$$

$$\frac{1}{\lambda} = (1.097 \times 10^7 \text{ m}^{-1}) \left(1 - \frac{1}{25} \right)$$

$$\frac{1}{\lambda} = (1.097 \times 10^7 \text{ m}^{-1})(0.96)$$

$$\frac{1}{\lambda} = 10531200 \text{ m}^{-1}$$

Step 2: Take the inverse of both sides to find λ .

$$\lambda = 9.50 \times 10^{-8} \text{ m}$$

Step 3: Convert to nm.

$$9.50 \times 10^{-8} \text{ m} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} = 95.0 \text{ nm} < 400 \text{ nm}, \text{ so not visible}$$

Procedure

Part I: Spectroscope Instructions

In this experiment you will use a spectroscope, a device to observe spectra, to measure and record both absorption and emission data. A diagram of the scope is shown below (Fig. 4).

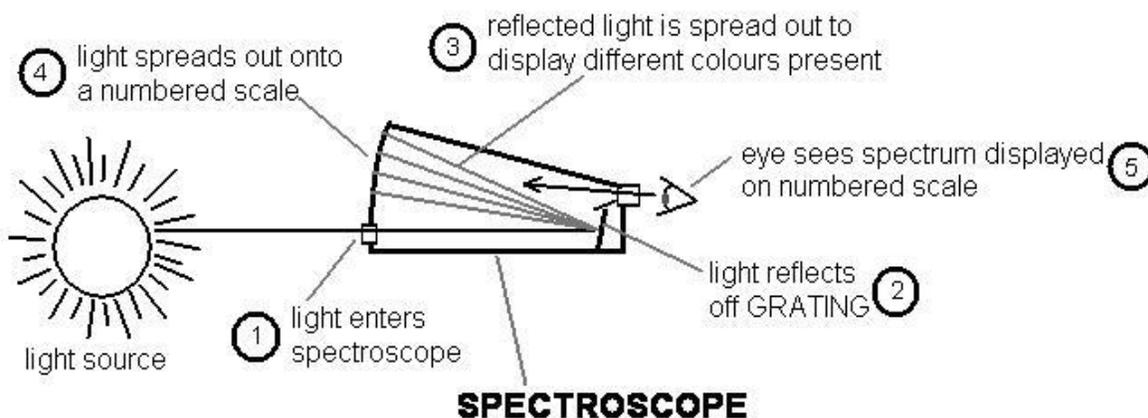


Fig. 4: Diagram of a spectroscope

(<http://wikieducator.org/images/f/f4/Chemistry - Observing Light Spectrum 3.JPG>)

To use the scope, look into the viewing hole on the smaller end and align the slit on the opposite end with a light source. Light enters the slit and strikes the grating, a piece of plastic that works like a prism. Most of the light passes through the grating to your eye, but part of it undergoes diffraction: it is broken up into its component wavelengths and projected back onto the scale. Through the grating you will see spectral lines superimposed on the scale from which you can read their approximate wavelengths.

Part II: Spectroscope Calibration

1. Using your spectroscope, look through the slit while pointing the grating at the mercury vapor lamp. You should see three bright lines on your scale: yellow, bright green, and blue. Record the scale positions on your data sheet as accurately as possible. More faint lines may be visible; do not record these. Since moving the box will shift the lines, try to be as consistent and still as possible.

2. Plot a calibration graph of the known wavelengths (x-axis) versus the scale readings (y-axis). Add a trendline and record the equation to use in Part III.

Part III: Spectral Analysis of Gas Lamps

1. Using your spectroscope, read and record the scale positions and colors of the emission lines from the helium lamp. Helium will have many lines. Record the brightest five that you see.

2. Using your trendline equation from your calibration graph in Part II, convert the scale reading for each observed line to wavelength in nm.

3. Repeat Steps 1-2 for the hydrogen lamp. Record the brightest three lines that you see.
4. Calculate the expected emission wavelengths for the Balmer series of hydrogen ($n_1 = 2$ and $n_2 = 3, 4, 5,$ and 6). Match your observed wavelengths to the closest expected wavelength to find n_2 for each. One of the boxes will be blank (you are calculating four wavelengths but observed only three).
5. Plot $1/\text{wavelength}$ versus $1/n_2^2$ for your three observed wavelengths. Determine R_H and compare it to the known value.

Part IV: Spectral Analysis of Flame Tests

1. Place a small quantity of NaCl crystal on the tip of a nichrome wire attached to a cork. You may need to wet the wire first in order to make the solid stick.
2. Using a Bunsen burner and holding the cork, position the wire so that the end holding the crystal is in the center of the flame. Meanwhile have your partner use the spectroscope to read and record on your data sheet the scale positions and colors for each observed emission line. You may need multiple samples to record every emission line.
3. Wash the wire with dilute hydrochloric acid and then deionized water.
4. Repeat Steps 1-3 with LiCl and SrCl₂ crystals. Be careful to not cross-contaminate the reagents.
5. Using the trendline prepared in Part II, convert each scale reading to wavelength in nm.

Part V: Spectral Analysis of Absorption Spectra

1. Using your spectroscope, observe the spectrum from a white light ordinary light bulb.
2. Place the test tube of KMnO₄ solution between the light bulb and your spectroscope. Read and record on your data sheet the wavelength region most strongly absorbed by the sample by shading the regions on the scale where visible light *can* be seen.
3. Repeat Step 2 with the solutions of CuSO₄ and CoCl₂.
4. Using the trendline prepared in Part II, convert each scale reading for the region *absorbed* to wavelength in nm.

Experiment 17—Data Sheet

Name: _____

Part II: Spectroscope Calibration

Mercury

| Color | Scale Reading | Wavelength (nm) |
|--------|---------------|-----------------|
| Blue | | 435.8 |
| Green | | 546.1 |
| Yellow | | 579.0 |

Trendline Equation (from graph): _____

Part III: Spectral Analysis of Gas Lamps

Helium

| Color | Scale Reading | Wavelength (nm) use trendline equation |
|-------|---------------|---|
| | | |
| | | |
| | | |
| | | |
| | | |

Show calculation for scale reading to wavelength:

Hydrogen

| Color | Scale Reading | Wavelength (nm) use trendline equation |
|-------|---------------|---|
| | | |
| | | |
| | | |

Show calculation for scale reading to wavelength:

| n_1 | n_2 | Calculated Wavelength (nm) use Rydberg's Equation | Experimentally Observed Wavelength (nm) from previous table |
|-------|-------|--|--|
| 2 | 3 | | |
| 2 | 4 | | |
| 2 | 5 | | |
| 2 | 6 | | |

Show calculation for calculated wavelength:

| Matched n_2 | $1/n_2^2$ | Experimentally Observed Wavelength (nm) from previous table | $1/\text{wavelength}$ (1/nm) |
|---------------|-----------|--|---------------------------------|
| | | | |

| | | | |
|--|--|--|--|
| | | | |
| | | | |
| | | | |

Trendline Equation (from graph): _____

Experimental R_H value: (m^{-1}) _____

Percent Error (%): _____
show calculation:

Part IV: Spectral Analysis of Flame Tests

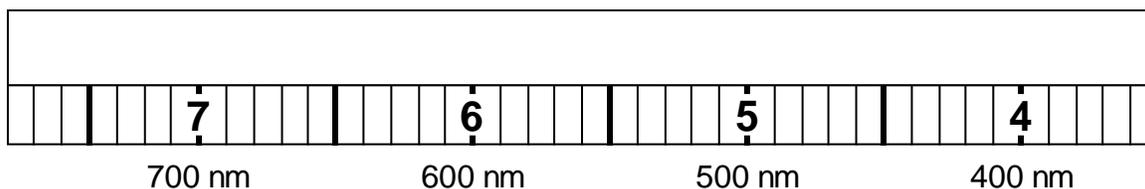
| | Color | Scale Reading | Wavelength (nm) Use trendline equation |
|-------------------|-------|---------------|---|
| NaCl | | | 4 |
| LiCl | | | |
| SrCl ₂ | | | |

Show calculation for scale reading to wavelength:

Part V: Spectral Analysis of Absorption Spectra

1. Color of $KMnO_4$ solution without spectroscope: _____

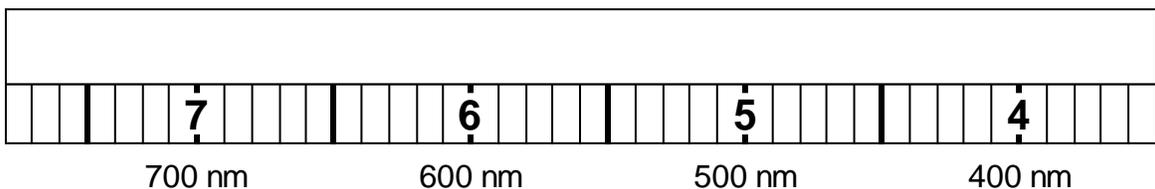
2. Regions where visible light was seen for $KMnO_4$:



3. Wavelengths absorbed (nm): _____ to _____

4. Color of CuSO_4 solution without spectroscope: _____

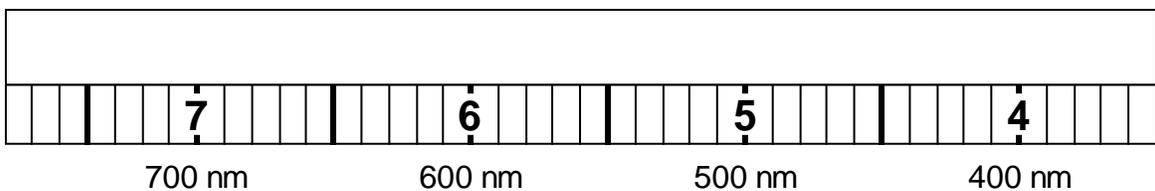
5. Regions where visible light was seen for CuO_4 :



6. Wavelengths absorbed (nm): _____ to _____

7. Color of CoCl_2 solution without spectroscope: _____

8. Regions where visible light was seen for CoCl_2 :



3. Wavelengths absorbed (nm): _____ to _____

Experiment 17—Post-Lab Assignment

1. Helium has many emission lines in the visible light region, though you observed only the most intense ones. Match your observed wavelengths from Part III to the published values below. Priority should be given to the most intense lines. Many of the boxes will remain blank.

| Wavelength (nm) | Intensity | Observed Wavelength (nm) | Wavelength (nm) | Intensity | Observed Wavelength (nm) |
|-----------------|-----------|--------------------------|-----------------|-----------|--------------------------|
| 388.9 | 1000 | | 471.3 | 40 | |
| 396.5 | 80 | | 492.1 | 50 | |
| 400.9 | 10 | | 501.6 | 100 | |
| 402.6 | 70 | | 504.8 | 15 | |
| 412.0 | 35 | | 541.1 | 50 | |
| 414.4 | 15 | | 587.56 | 1000 | |
| 438.8 | 30 | | 587.59 | 10 | |
| 443.8 | 10 | | 656.0 | 100 | |
| 447.1 | 100 | | 667.8 | 100 | |
| 468.6 | 300 | | 706.5 | 70 | |

2. For NaCl, calculate the percent error between your measured emission line's wavelength in Part IV and the tabulated value of 588.9 nm.

3. Using your measured emission lines in Part IV, calculate the energy in J from the observed wavelength for NaCl, LiCl, and SrCl₂.

4. Based on your data for Part V, explain why KMnO_4 solutions appear visibly purple. (Hint: Careful! Remember that the process responsible for causing the visible color of a solution is a different process than the colors seen in the gas discharge tubes or flame tests).

5. The amount of energy required to completely remove an electron from a hydrogen atom can be found by assuming it is being taken from the $n = 1$ level to the $n = \infty$. Calculate this amount of energy, in J. (Hint: what numerical value does $1/\infty$ approach?)

Experiment 17—Pre-Lab Assignment

Name: _____

For all calculations, show all work and draw a box around the final answers.

1. The lab mentions four equations. Which one of these equations works **only** for the hydrogen atom?

2. The wavelength of green light is around 510 nm. What is the frequency of green light, in Hz? What is the energy of a single photon of green light, in J?

3. If an electron in a hydrogen atom falls from $n = 3$ to $n = 1$, is energy absorbed or emitted? Calculate the wavelength of the light associated with this transition, in nm. In what part of the electromagnetic spectrum would this wavelength fall?

4. Explain the difference between an absorption and an emission spectrum for an element