

HYDROGEN EMISSION AND ABSORPTION SPECTRA

The early part of the 20th century is known as *the golden age of physics* because significant progress was made in multiple areas of physics, including the birth of quantum mechanics. The development of quantum theory to explain electron arrangement in the atom is a case study of how scientific understanding changes with experimental data. Advances in the late 19th century paved the way for advances in atomic theory in the early 20th century. For example, Mendeleev noticed repetitive patterns in elements of increasing mass, Thomson discovered the positive and negative nature of matter, and Rutherford's gold foil experiment revealed that most of an atom's mass was located in a small, positively-charged central nucleus. Rutherford's work raised a major question in the first decades of the 20th century: how is negative charge distributed within an atom?

As shown in the line emission spectrum for hydrogen (Figure 1), only certain colors of light are emitted when an element is energized. This light pattern is unique to each element. Balmer devised a mathematical formula to describe the energy of this light. Balmer's original formula related the four wavelengths of visible light present in the hydrogen line emission spectrum with the integers (m) and (n) and a constant (k):

$$\lambda = k \left(\frac{m^2}{m^2 - n^2} \right)$$



Figure 1. Partial versus continuous spectrum

The formula reliably predicted the observed wavelengths as well as wavelengths outside of the visible spectrum, but there was no theoretical basis to explain the relationship among variables in the formula. Rydberg then related the equation to wavenumber ($1/\lambda$) and an empirical constant (R) known as the Rydberg constant.

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

Bohr applied the theory of energy levels to the modified equation. When describing the visible hydrogen line emission spectra, the value for final energy level (n_f) is always 2 because all four wavelengths are produced from an excited electron falling from a higher energy level to the second energy level. The value for n_i is the initial excited energy level greater than 2, such as level 3, 4, 5, or 6. The value for R is the Rydberg constant which equals $1.09737 \times 10^7 \text{ m}^{-1}$. Bohr combined the Rydberg modification of Balmer's formula, Rutherford's atomic model, and the work of Planck and Einstein to propose an explanation of the hydrogen line emission spectrum. He proposed that electrons can only move from one "orbit" to another when discrete amounts of light energy are absorbed. Once electrons absorb just the right amount of energy, they could jump to a higher-energy orbit. Bohr hypothesized that the spectral pattern could only arise if electrons were restricted to a series of set orbits positioned at different distances from the nucleus, and orbit distance was directly related to energy. Bohr expressed the energy of this orbit series in terms of the electron level (principal quantum number) shown in Figure 2.

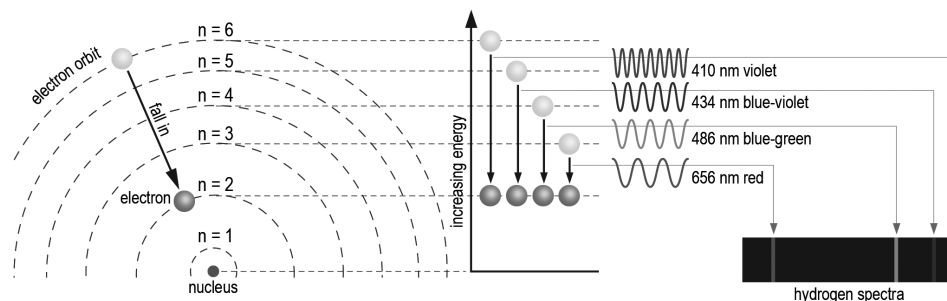


Figure 2. Bohr's model proposed an explanation for hydrogen's line emission spectrum

While Bohr's model only works for atoms with only one electron, it provides the basis for two enduring ideas:

- Electrons are arranged around the nucleus according to their energy.
- Emission spectra are related to electrons' absorbance and emission of discrete amounts of energy as they transition between energy levels.

Today, quantum theory explains how the visible hydrogen line emission spectrum is produced. When electrons are excited to *orbitals* in the third, fourth, fifth or sixth energy levels ($n = 3, 4, 5$, or 6) then return to the second energy level ($n = 2$), the atom releases photons with wavelengths corresponding to the energy difference between levels.

In the first part of this investigation, you will use a fiber optics cable to channel light into a spectrometer and determine the wavelengths of light produced by hydrogen's line emission spectrum. You will use the Balmer-Rydberg formula to predict the wavelength values and compare them to the experimental values. The measured wavelengths will also be used to graph wavenumber versus energy level value to experimentally determine the value of Rydberg's constant.

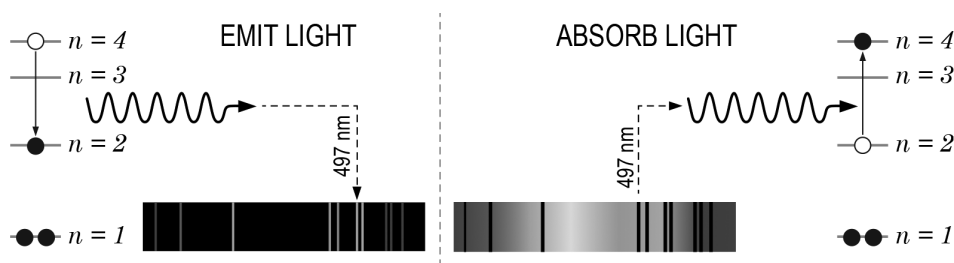


Figure 3. Emission is a high-to-low energy transition; absorption is a low-to-high transition

In the second part of this investigation, you will observe the absorption spectrum of the Sun. As shown in Figure 3, emission describes the energy released when an electron moves from an excited state to a lower energy state, while absorption describes the energy taken in by an electron that enables its movement from a lower to higher energy state. Nuclear reactions fusing hydrogen into helium in the Sun's core convert four million tons of matter into energy every second. As a result, the Sun emits nearly all wavelengths of energy across the electromagnetic spectrum, with the greatest intensity in the portion we call *sunlight*. Sunlight includes the visible spectrum, ultraviolet radiation (UV), and infrared radiation (IR). When you observe sunlight with the fiber optics cable, you will see a series of minor peaks and valleys in the sunlight region of the electromagnetic spectrum. The valleys represent absorbance wavelengths. The absorbance wavelengths are produced when elements and compounds present in the solar atmosphere or Earth's local atmosphere selectively absorb the energy released by the Sun. Scientists can determine the atmospheric composition of a distant star by matching its absorbance spectra to the spectra of known substances. For example, when observing our Sun's absorption spectrum you can expect to see valleys or absorbance lines at the same wavelengths as the hydrogen gas emission lines.

Objectives

- Compare predicted hydrogen line emission wavelengths with observed wavelengths.
- Relate the line emission spectrum of hydrogen to quantized energy level transitions.
- Explain the difference between emission spectra and absorption spectra.
- Experimentally determine Rydberg's constant.

Materials and Equipment

- Data collection system
- Spectrometry software
- Spectrometer
- Fiber optics cable
- Ring stand with clamp
- White sheet of paper
- Hydrogen gas spectrum tube
- Spectrum tube power supply

Safety

Follow these important safety precautions in addition to your regular classroom procedures:

- Use caution around the spectrum tube and its high-voltage power supply. Your instructor will likely operate the spectrum tube, but in case of emergency, know the location of the power switch on the power supply.
- Gas spectrum tubes get hot. Do not allow the spectrum tubes to contact any other material. Do not touch gas spectrum tubes with your bare hands.

Procedure

Part 1: Wavelengths from the hydrogen line emission spectrum

1. Connect the spectrometer to your device. Insert the fiber optics cable in the cuvette holder according to the appropriate spectrometer shown in Figure 4.

NOTE: The UV-Vis Spectrometer is powered by the USB cable when viewing emission spectra in Light Analysis mode. The unit does not need to be turned on and the power supply is not required.

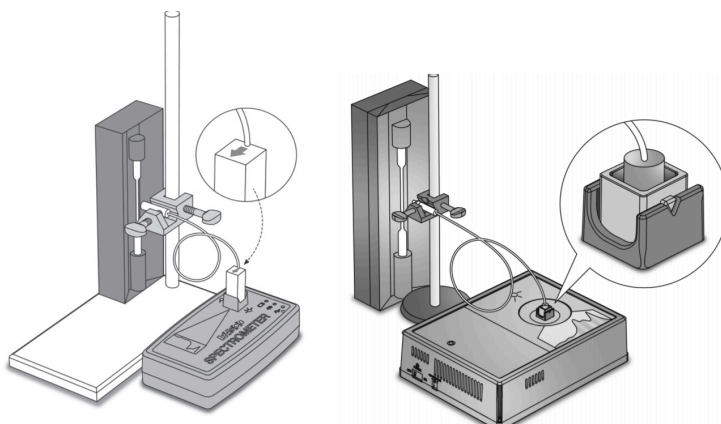









Figure 4. Insert the fiber optics cable into the Wireless Spectrometer (left) or UV-Vis Spectrometer (right)

2. Open the Spectrometry app. Select **Analyze Light**  at the top.
3. Attach the clamp to the ring stand and secure the fiber optics cable in the clamp as shown. Do not over-tighten the clamp.
4. Position the end of the fiber optics cable very near, but not touching, the hydrogen spectrum tube.
5. Turn on the lamp. Click  to start recording data in Spectrometry.
6. Reposition the fiber optics cable to directly align with the beam of light in the gas tube as needed to get the highest light intensity possible.
7. Once you have found the ideal position, select **Auto Set** under **Integration Time** to the left of the graph display. Wait for the software to finish determining integration time.

- Adjust **Smoothing** if necessary, then stop recording data. Select **Source #1** to rename the run to **H-lamp**.
- Under **Reference** at the bottom, click **None** then select **Hydrogen** to show reference emission wavelengths for hydrogen. The four black lines that appear in the visible light region are the expected emission lines for hydrogen gas.
- Click  to add a Coordinates Tool to each peak near the four reference lines in the visible spectrum. Use the Coordinates Tool to measure the experimentally determined wavelengths. Record the results in Table 1. If the violet-region peak is not easily visible, drag each axis to manually scale the x- and y- axes. If the peak is not distinguishable from background noise, do not choose a peak.

Part 2: Evidence of hydrogen in the solar absorbance spectrum

- Remove the fiber optics cable from the clamp.
- Take the spectrometer with fiber optics cable, a sheet of white paper, and your device outside (unless otherwise directed by your instructor).
- Place the sheet of paper in full sunlight.
- Click  to start recording data. Position the fiber optics cable very near, but not touching, the paper (by hand) to reflect solar light into the spectrometer. Experiment with positioning until you achieve the highest intensity signal.
- Hold the cable position steady and click **Auto Set** under **Integration Time**.
- Increase the **Number of Scans to Average** to improve the distinctions between peaks and valleys, then click  to stop recording data. Do not adjust Smoothing and set the **Reference** to **None**.
- Rename the run to: **Solar spectrum**. Click  to display both data runs at the same time.
- Click  to add a Coordinates Tool to identify the hydrogen reference lines that align perfectly with the **H-lamp** data. You may not find solar spectrum matches for all four H-lamp wavelengths. Record results in Table 1.
- Compare the hydrogen emission data with the solar absorbance data. Record your observations as you answer the first question below Table 2.
- Use wavelengths from Table 1 to complete Table 2 and questions in the **Data Collection** section before moving on to the **Questions and Analysis** section.

Data Collection

Table 1. Visible Light Energy Transitions in the Hydrogen Atom

Photon color (& energy transition)	H-lamp wavelength, λ (nm)	Frequency, ν (s^{-1})	Energy, E (J)	Solar spectrum match? (Yes or No)
Red ($n = 3$ to $n = 2$)				
Cyan/blue-green ($n = 4$ to $n = 2$)				
Blue ($n = 5$ to $n = 2$)				
Violet ($n = 6$ to $n = 2$)				

Table 2. Calculated Values for Visible Light Emission in the Hydrogen Atom

Initial energy level, n_i	Final energy level, n_f	Predicted λ (nm)	Percent error (%)	Excited energy level value	Wavenumber (m^{-1})
$n = 3$	$n = 2$				
$n = 4$	$n = 2$				
$n = 5$	$n = 2$				
$n = 6$	$n = 2$				

- Describe your observations of the hydrogen emission spectrum compared to the solar absorption spectrum.
- Use the following equations to calculate the frequency and energy of the emitted photons; show work for one wavelength and enter answers in Table 1: $c = \lambda\nu$ ($c = 3.00 \times 10^8$ m/s) and $E = h\nu$ ($h = 6.63 \times 10^{-34}$ J·s).
- Use the Balmer-Rydberg equation to calculate the predicted wavelengths (in nm) for the four energy transitions that produce the hydrogen emission lines in the visible spectrum. Show your work for one transition in the space provided and enter your answers in Table 2. (The accepted value for Rydberg's constant, $R = 1.09737 \times 10^7 \text{ m}^{-1}$.)

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

- Calculate the percent error for each experimentally determined wavelength and enter results in Table 2. Show one sample calculation in the space provided, then comment on the accuracy of your data.

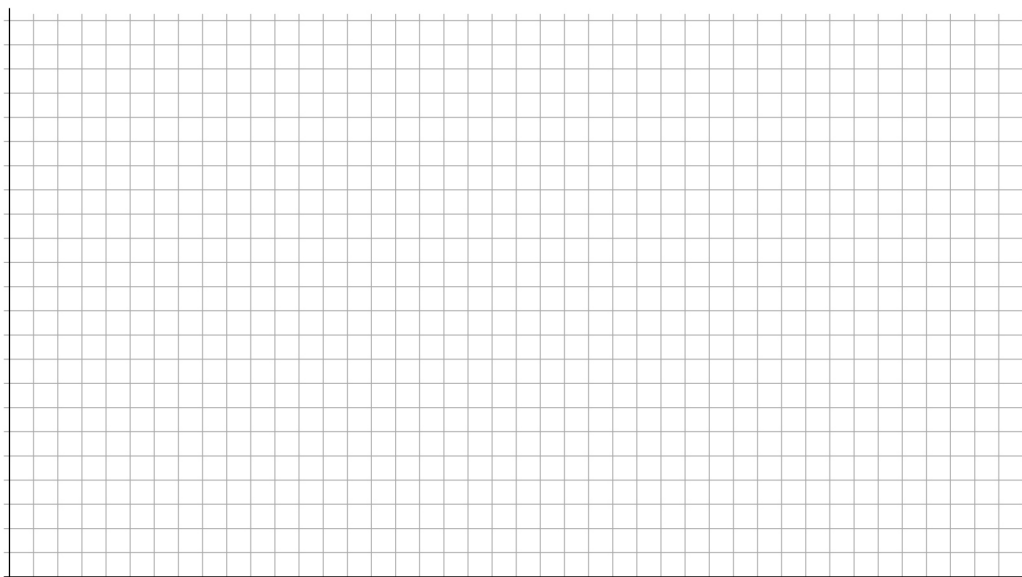
5. Use the following equation to calculate the reciprocal squared excited energy level value for each energy transition; record your answers in Table 2 and show one sample calculation in the space provided:

$$\text{Excited energy level value} = \frac{1}{n_i^2}$$

6. Each photon emission can be described by the number of waves per meter, or, *wavenumber*. Use the following equation to calculate the wavenumber (in m^{-1}) for each energy transition and enter your results in Table 2; show your work for one calculation in the space provided:

$$\text{Wavenumber} = \frac{1}{\lambda} \times \frac{10^9 \text{ nm}}{1 \text{ m}}$$

7. Use a graphing application to create a graph of wavenumber versus energy level value (from Table 2) and apply a least squares linear fit. Sketch your graph below. Include a title, label both axes, use appropriate numeric ranges and intervals, and include units. Show the best fit line along with the linear equation that includes the values for slope and y-intercept.



Questions and Analysis

1. How does the interpretation of an emission spectrum differ from an absorption spectrum when looking for the presence of an element? Does your data confirm the presence of hydrogen in the solar atmosphere? Why or why not?
2. According to quantum theory, electrons that make energy level transitions that are far apart require greater absorption energy than electrons that make transitions between energy levels that are closer together. Do your results validate quantum theory? Use data and calculations from this investigation to support your answer.
3. When performing the emission calculations in this investigation, why was the final energy level always $n = 2$? In what case would $n = 2$ be the initial energy level?
4. Slope describes the relationship between the x and y variables on a graph. Rydberg's constant quantifies the relationship between wavenumber and energy levels. How does the absolute value of the slope derived from your data compare to the accepted value for R ? Discuss your answer in terms of percent error.
5. Predict the wavelength of a photon emitted when an electron transitions from $n = 2$ to $n = 1$ in a hydrogen atom. Show your work. Is this photon more energetic or less energetic than those observed in the wavelengths in Table 1? Explain why this electron transition did not appear in the visible hydrogen line emission spectrum.
6. Does your answer to the previous question violate the quantum theory statement in question 2? Why or why not?
Hint: Recall that the distance between energy levels becomes smaller as distance from the nucleus increases.