# Quantum States for the Visible Hydrogen Atomic Emission Spectrum and the Rydberg Equation

### Goal and Overview

Color, wavelength, and frequency of light in the visible region of the electromagnetic spectrum will be investigated using a Spec 20 spectrometer. The visible emission spectrum of excited helium will be used to assess the accuracy of the spectrometer that will be used to measure the visible emission lines of excited hydrogen atoms. The principal quantum numbers associated with the visible H\* emission wavelengths will be verified and an experimental value of the Rydberg constant will be extracted from graphical analysis of the H\* emission wavelengths.

## **Objectives and Science Skills**

Explain and use the relationship between photon wavelength and energy, both qualitatively and quantitatively.

Understand and explain atomic absorption and emission in relation to allowed energy levels (states) in an atom as well as their relationship to photon wavelength and energy. Evaluate the precision of a spectrometer by comparing measured He\* emission lines to literature values.

Observe atomic H\* line spectra, fit data to the Rydberg equation, and compare experimental results to theoretical values.

Analyze and discuss factors that limit the precision of the results.

# Suggested Review and External Reading

Reference materials and textbook sections covering spectroscopy, atomic theory, atomic emission, and graphical analysis

## Introduction

Spectroscopy, the study of the interaction of light with matter, has played a fundamental role in the development of atomic and molecular theory. Most modern chemistry, biology, geology, astronomy, and physics labs use some type of spectroscopy to qualitatively and/or quantitatively analyze matter.

The wave nature of light is evident in its oscillating perpendicular electric and magnetic fields (electromagnetic radiation); these fields may interact with the electric and magnetic properties of matter in a variety of ways. The photon, which is used to describe the particle

nature of light, carries a "packet" of energy that is proportional to the radiation frequency, v, and inversely proportional to its wavelength,  $\lambda$ .



 $E_{photon} = E_{h\nu} = \frac{hc}{\lambda}$ , where  $h = 6.626 \times 10^{-34}$ J · s and  $c = 2.998 \times 10^8$ m/s

Each electron in the atom resides in an orbital of principal quantum number, n, with a discrete, well-defined energy. An atom may absorb a photon's energy and transition from a lower energy state to a higher-energy "excited" state ( $n_f > n_i$  and  $\Delta E_{atom} > 0$ ). Energy may be emitted as a photon when an excited atom falls from a higher energy state to a lower one ( $n_f < n_i$  and  $\Delta E_{atom} < 0$ ). The photon energy must match exactly the energy difference between  $n_i$  and  $n_f$ .



This experiment will focus on the atomic emission by excited helium atoms (He\*) and excited hydrogen atoms (H\*) in the visible region of the electromagnetic spectrum. Discrete emission lines specific to each element are observed because each type of atom has its own unique, quantized orbital energies.

The most abundant isotope of the hydrogen atom consists of one proton and one electron. H\* emission lines (energies) are given by the Rydberg equation, which was first expressed by Johannes Rydberg in 1888 and then theoretically derived by Niels Bohr in 1913.

$$\Delta E_{atom} = -R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right), \text{ where } R_H = \frac{2\pi e^4 m}{h^3 c} = 2.18 \times 10^{-18} \text{ J}$$

The emission spectrum of H\* has been divided into a number of series. The transitions in each series share a common  $n_f$ , and some are named (Lyman series,  $n_f = 1$ ; Balmer,  $n_f = 2$ ; Paschen,  $n_f = 3$ ; Brackett,  $n_f = 4$ ; Pfund,  $n_f = 5$ ; and, Humphreys,  $n_f = 1$ ). The four lowest-energy electronic transitions in the Balmer series ( $n_f = 2$ ;  $n_i = 3, 4, 5, and 6$ ) correspond to visible emission wavelengths.





# Equipment List

Spec 20 spectrophotometer Lucite rod Table-top spectrometer Helium discharge tube/high voltage lamp Hydrogen discharge tube/high voltage lamp

## Procedure

The experiment consists of two main parts. Part 1 allows you to investigate the visible region of the electromagnetic spectrum using a Spec 20 in a non-traditional way. In Part 2, you will measure the He<sup>\*</sup> emission lines in the visible region to gauge the accuracy of the table-top spectrometer that you will use to observe H<sup>\*</sup> emission wavelengths. Using the H<sup>\*</sup> emission data, you will verify  $n_f$  for the observed emission series and determine an experimental value of the Rydberg constant,  $R_H$ , graphically.

Part 1. Visible light: quick investigation of wavelength, color, intensity

#### Caution

A Lucite rod is taped in the sample holder of your Spec 20. Please do not touch or remove or twist the rod. It is oriented to transmit light up to you rather than to the detector. Do not use the knobs on the front of the instrument. Only use the wavelength adjust knob.

1. Use the wavelength adjust knob to change wavelength while looking at the rod. Get a quick sense of how the color changes over the 400 – 700 nm range.

2. Write down the color of light you observe at 20-nm intervals from 400 to 700 nm. Broadly classify the colors as violet, blue, green, yellow, orange, or red.

3. Record the boundary wavelength between different colors and the wavelength at which each color shows its maximum intensity. These wavelengths can be given to the ones place.

Color	Wavelength (nm)			
Violet	400 - 440			
Blue	460 - 480			
Green	500 - 560			

Yellow	580
Orange	600 - 620
Red	640 - 700

## Part 2. Atomic Emission

# Part 2a. Handheld Spectrometers (if available)

Point the slit of a handheld spectrometer at a fluorescent light and look through the eyepiece. Bright blue and green lines are due to excited mercury atomic emission. Adjust the side shutter on the spectrometer to control the amount of light illuminating the wavelength scale. More light makes it easier to read the wavelength scale but harder to see the spectral lines.

Parts 2b and 2c. He\* emission (spectrometer "calibration") and H\* emission (graphical analysis)

#### Caution

Please do not touch the gas-discharge lamps, the housings around them, or the power supply connections and cords.

Please keep the lamps off as much as possible; only turn a lamp on when you are observing the emission lines.

Please make sure to push the switch on the variable power supply to 120 V or OFF (not to 220 V), and please do not change the power setting.

Please handle the spectrometer carefully and gently; do not adjust the slit width.



The light emitted by the excited He<sup>\*</sup> or H<sup>\*</sup> atoms in the gas-discharge lamp enters the spectrometer through a narrow slit. A diffraction grating disperses the light into its constituent spectral lines, which are superimposed on a wavelength scale (e.g.,  $6.60 \times 10^{-5}$  cm or 660 nm).

When you look through the eyepiece, you should see the very bright light from the gas discharge tube coming through the slit on the left and the colored visible emission lines to the right. You may have to illuminate the wavelength scale with a flashlight to read the values.

Position your head so that an intense emission line falls on the scale at its approximate expected value and keep a constant line of sight through the eyepiece; the line positions shift on the scale if you move your head.

Record your measured experimental wavelengths to two significant figures (uncertainty of  $\pm 10$  nm).

#### Part 2b. He\* Emission

Helium Emission Lines				
Color	λ (nm)			
blue-violet	447.1			
blue-green	471.3			
green	492.2			
green	501.5			
yellow	587.5			
red	667.8			
red	706.5			
red	728.1			

4. Point the table-top spectrometer towards the He gas-discharge tube and position the slit so that you observe colored lines on the scale. It may be helpful to use the strong yellow line at 587.5 (590) nm to adjust your line of sight.

Write down the wavelength ( $\pm 10$  nm) and color of each observed spectral line.

You might not be able to see all of the lines, particularly if they lie near the lower or upper limits of the visible region of the spectrum. A few lines are very close to each other, making it hard to distinguish them individually. 5. Compare your measured wavelengths with the known emission lines (which are given to four significant figures). How well do the observed emission lines match the theoretical values?

6. Calculate the percent error in the experimental He\* emission wavelengths to two significant figures. How would you describe the accuracy of the spectrometer, and how does the accuracy relate to the precision in your measurements?

Part 2c. H\* emission

Hydrogen Emission Lines

Color	λ (nm)		
violet	410.1		
blue-violet	434.0		
blue-green	486.1		
red	656.2		

7. Carefully rotate the table-top spectrometer so that you can view the emission from the hydrogen gas-discharge tube. The red line at 656.2 (660) nm or the blue-green line at 486.1 (490) nm are good choices for line-of-sight positioning. Record the wavelength of each emission line you observe to ±10 nm and the color of each.

Try to see all four lines; you must see at least three.

Note: excited H\* atoms give rise to the line spectrum; any multi-colored bands you see are due to excited H<sub>2</sub> molecules (which have allowed vibration levels within each electronic level).

8. Calculate the photon energy associated with each emission line in Joules (to four significant figures for the theoretical wavelengths and to two for your experimental values).

$$E_{h\nu} = \frac{hc}{\lambda}$$
, where  $h = 6.626 \times 10^{-34} \text{J} \cdot \text{s}$  and  $c = 2.998 \times 10^8 \text{m/s}$ 

9. Calculate the percent error in each to two significant figures. Do you expect large percent errors? What limits the precision and accuracy of your values?

Graphical analysis of H\* emission – the Rydberg equation

The Rydberg equation can be written in terms of positive photon energies ( $E_{h\nu} > 0$ ) and then rearranged in the form of a straight line equation (y = mx + b).

$$E_{h\nu} = |\Delta E_{atom}| = R_H \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \rightarrow E_{h\nu} = -R_H \left(\frac{1}{n_i^2}\right) + \frac{R_H}{n_f^2}$$

10. Plot  $E_{hv}$  for each emission line on the y-axis vs. its corresponding  $\frac{1}{n_i^2}$  value on the x-axis. You should have three or four data points. The lowest-energy photon (longest wavelength) corresponds to the lowest-energy electronic transition ( $n_i = 3 \rightarrow n_f = 2$ ). Make sure that you assign each energy to the correct electronic transition ( $n_i = 6, 5, 4, \text{ or } 3 \rightarrow n_f = 2$ ). The points should fall on a straight line.

Example da	ata					x-axis	y-axis
$\lambda$ , lit (nm)	color	$\lambda$ , exp (nm)	n <sub>f</sub>	n <sub>i</sub>	$1/n_{f}^{2}$	$1/n_{i}^{2}$	E (J)
410.1	violet	410	2	6	0.250	0.0278	4.8E-19
434.0	blue-violet	430	2	5	0.250	0.0400	4.6E-19
486.1	blue-green	490	2	4	0.250	0.0625	4.1E-19
656.2	red	650	2	3	0.250	0.111	3.1E-19

11. Draw the best-fit line through the points (or use Excel®, Google Sheets®, etc.), and determine the slope, which should be negative, to three significant figures. Calculate your experimental value for the Rydberg constant ( $R_{H,exp} = -slope$ ) and the percent error relative to the literature value of  $R_H = 2.18 \times 10^{-18}$  J to three significant figures.

12. Determine the value of the y-intercept to three significant figures and calculate the percent error relative to its expected value of  $\frac{R_H}{n_f^2} = \frac{R_H}{2^2} = 5.45 \times 10^{-19}$  J.

13. Determine the value of the x-intercept, the point at which the best-fit line crosses the x-axis. At this point,  $E_{hv} = 0$  and  $n_f = n_i = 2$ , so  $\frac{1}{n_i^2}$  should  $\frac{1}{2^2} = 0.250$ . Calculate the percent error to three significant figures.

Results / Sample Calculations

Complete the online inlab or write a lab report as directed by your TA. %errors in He\* and H\* emission lines

Submit your graph with best-fit line Experimental values for slope,  $R_H$ , y-intercept, and x-intercept; %errors

## **Discussion Questions and Review Topics**

Discuss your Spec 20 color-wavelength observations. What did you notice about the wavelength range of certain colors? Their relative intensities? How does this relate to biological topics such as human color vision, photosynthesis and sunlight, etc.? How accurate and how precise were your results for the He\* and H\* emission using the table-top spectrometer? Are deviations from the literature values due to equipment limitations, or do the atoms emit different wavelengths under different experimental conditions?

Did the H\* emission lines in the visible region of the spectrum correspond to  $n_f$  = 2? How closely did your experimental results match the expected values? How do you think your plot would have differed if you had chosen the wrong  $n_f$ ?