

Experiment 2: Energy Levels and Spectra—Atomic Spectroscopy

Objectives: To observe the emission spectrum of the hydrogen atom and to determine by experiment the ionization energy of the H atom.

References: *IMT* Chapter 3. Brown, *et al.*, pp. 183-193

Logistics: Work in pairs.

Prelaboratory

preparation: See the general requirements listed in the introductory pages. Read over the experiment carefully—more than once—before coming to lab. Look up the ionization energy of the hydrogen atom. Use this value (in units of J) for the *Rydberg constant*, R_H , to calculate the wavelength of light emitted by an electron falling from the $n=2$ to the $n=1$ electronic energy level in the hydrogen atom. What color of light is associated with this wavelength?

Introduction

In this experiment and the next, you will see how *spectroscopy*, the measurement of light absorption and emission by atoms and molecules, can yield important information about atomic and molecular structure.

In Part A of this experiment, you will study the energy levels of the hydrogen atom by observing its emission spectrum, that is, the light given off as an excited hydrogen atom's single electron falls from a higher to a lower level. From your data, you will determine the ionization energy of the hydrogen atom, also called the *Rydberg constant*, R_H . In Part B, you will take a look at how the electronic states of hydrogen can be interpreted in terms of probability.

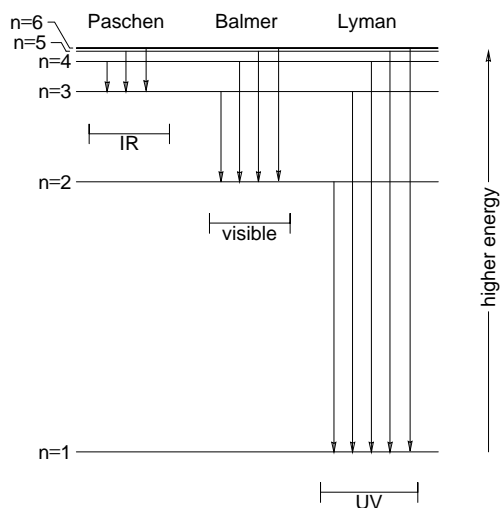
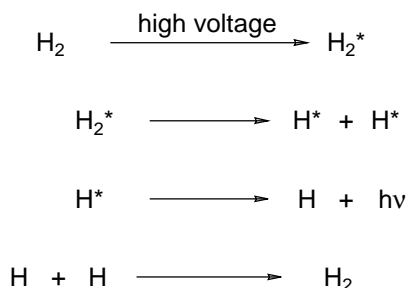


Figure 1. Several possible emissions of excited state hydrogen atoms. (Not all have the same probability of occurring, however.)

Part A

You will be using a hydrogen gas discharge tube (similar to a neon sign, but with hydrogen in it instead of neon), which generates hydrogen atoms in a variety of excited states:



Note that the initial blast of energy from the high voltage gives an excited *molecule* (indicated with an asterisk). This is simply an H_2 molecule with lots and lots of energy, both vibrational and electronic. In fact, there is so much energy in this molecule that in the next instant it breaks apart into two excited *atoms*. Other than translational energy, hydrogen atoms can only be excited in one way: their single electron must be in some orbital above the $1s$ orbital, for example in the $2s$, $4d$, or even $10f$ orbital. Almost immediately, this electron falls to a lower orbital and gives off a photon of light. The energy of this light is related to its frequency by Planck's constant:

$$E = h\nu$$

where h is Planck's constant, and ν is *nu*, the frequency of light. The electron will continue to fall, step by step, until it reaches the $1s$ state and can fall no further (the atom is in its *ground* state). Thus, a single excitation may lead to a whole shower of photons being emitted.

Once the atoms are in their ground state, two H atoms find each other and recombine to produce H_2 molecules again (giving off heat, which is another reason you should be careful) and starting the whole process over again.

The only step we will observe of all of these is the third step, the falling of the electron, because only that one gives off light. Some of the possibilities are shown in the diagram below:

It turns out that the only transitions which can be distinguished by the human eye are those from levels 6, 5, 4, and 3 to the $n = 2$ level. These transitions, the first four lines of the **Balmer series**, are the ones you will observe. All of the other possible transitions involve light that has too little energy to see (infrared) or too much (ultraviolet).

Note that the energy levels are not evenly spaced. They start at a negative value and increase as $1/n^2$, finally approaching 0. Theoretically, the energy levels of the hydrogen are given by:

$$\epsilon_n = -R_H \left(\frac{1}{n^2} \right) \quad (1)$$

Well, that's all fine *theoretically*, but your goal in this experiment is to determine the value of R *experimentally*. That is, now is your chance to see if what you've learned is really true. Your goal will be to use your observations to determine the value of the Rydberg constant, R_H .

Here's how you will get it: You will determine the wavelength (λ) of the light corresponding to the Balmer series, where $n_l = 2$ and $n_u = 6, 5, 4$, and 3 . Using the relationships $v\lambda = c$ (the speed of light, 3.00×10^8 m/s) and $E_{\text{photon}} = h\nu$, you will determine the energy of the photon associated with each of the four emissions.

Since the energy of the photon is simply the *difference* in energies of the two levels involved, we have:

$$E_{\text{photon}} = -R_H \left(\frac{1}{n_u^2} \right) - -R_H \left(\frac{1}{n_l^2} \right) = R_H \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right) \quad (2)$$

By inserting $n_u = 6, 5, 4$, and 3 and $n_l = 2$, you will get four measurements of R_H , which should all be pretty close to each other. You will average these values to get your experimental value for R_H .

Note that R_H is also the *ionization energy* of the ground state ($1s$) H atom, since to get that electron *out* you would have to go from $n = 1$ to $n = \infty$, that is,

$$\Delta E_{\text{ionization}} = E_{\infty} - E_1 = -R_H \left(\frac{1}{\infty^2} \right) - -R_H \left(\frac{1}{1^2} \right) = R_H$$

Thus, you will also be determining the ionization energy of the hydrogen atom in this experiment.

Safety Precautions to Note

Avoid touching the electrodes of the discharge tube power supply (may be up to 5000 Volts!). Do not touch the lamps, as they become very hot when used due to all those emissions in the infrared.

Procedure for Part A

The apparatus (a *spectroscope*) is shown in Figure 2.

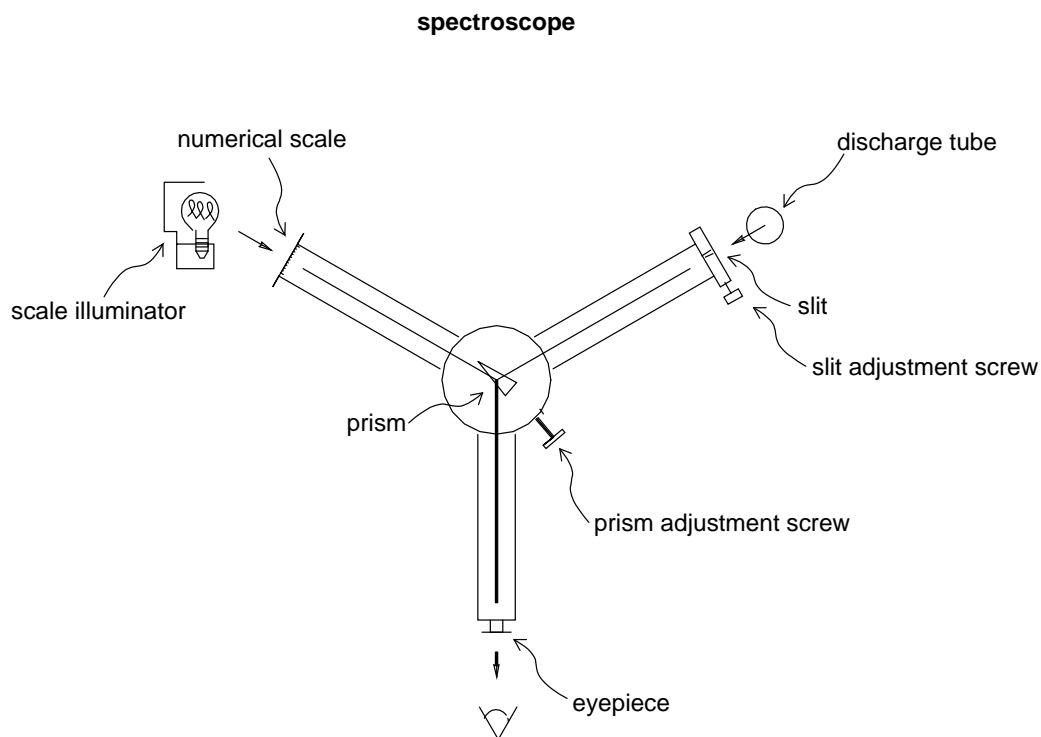


Figure 2. Diagram of a spectroscope. Light from the discharge tube goes through a slit, is separated into bands of color by the prism, and is observed through the eyepiece. A scale, projected through a third arm, allows a correlation to wavelength.

You will only be able to see a small portion of the visible spectrum at any given time. By turning the spectrum scan knob, you will scan through the entire spectrum. The auxiliary lamp at left is to light up a numbered scale which you will use to take readings on the spectral lines. The scale is not linear with respect to wavelength. You will use a graph available in the lab to correlate the scale reading with the actual wavelength.

Hydrogen and helium discharge tubes will be available in one of the hoods in the lab. Several other lamps will be available for your enjoyment, as well.

CAUTION: DO NOT TOUCH THE POWER SOURCE OF 5000 VOLTS!

1. Calibration (using a **helium** tube)

The spectroscope needs to be calibrated because the scale readings are dependent on the position of the prism. The calibration is carried out by lining up the bright yellow line in the helium spectrum with a scale reading of 1.80. We will try to adjust the prism so that this yellow line will be close to 1.80, but you may need to make a small correction.

First line up the spectroscope with the helium tube to get as bright a spectrum as possible. (Move the spectroscope, not the light source.) Then focus the eyepiece to get sharp lines. Turn on the scale illuminating light. A lighted scale should become visible. Finally, adjust the slit as necessary to sharpen the lines.

Turn the prism adjustment screw on the front of the spectroscope to bring the yellow line into the center of the field of view. Read and record the position of this line (notify the instructor if the line is not in the range 1.60–2.00).

2. Hydrogen Spectrum

UNPLUG THE POWER SOURCE and switch to the hydrogen tube. Set up the spectroscope so that you can see the lines from the hydrogen tube to best advantage. Adjust the slit as necessary to get the sharpest lines.

The hydrogen *atom* spectrum consists of 4 relatively strong lines due to the Balmer series. Superimposed on this spectrum is a more complicated background “hash” due to all of the excitations of H_2 *molecules*. Concentrate your efforts on the strong lines only. Obtain scale readings for these lines (one of the lines is near the ultraviolet and is somewhat difficult to see), reporting your results on the report form provided. Unplug the power source when you are finished.

Part A Data Analysis

Using the correlation chart provided in lab, determine the wavelength of light of each of the lines you observed. Also calculate the frequency, ν , (in s^{-1}) and energy, E (in Joules), corresponding to each line. Based on Figure 1, determine the level numbers u and l for each line. Then use Equation 2 to get a value of R_{H} from each line. Determine the average value for R_{H} . Express this value in both Joules and kJ/mol.

Part B

The actual solution to the Schrödinger Equation is shown below:

$$\Psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) \times \Theta_{lm}(\theta) \times \Phi_m(\varphi) \quad r \text{ radial or "altitude", } \theta(\text{theta}) \text{ latitude, and } \varphi(\text{phi}) \text{ longitude}$$

$$R_{nl}(r) = (2/na_o)^{3/2} \left(\frac{(n-l-1)!(n+l)!}{2n} \right)^{1/2} (2r/na_o)^l e^{-r/na_o} \sum_{j=0}^{n-l-1} \frac{(-2r/na_o)^j}{j!(n-l-j-1)!(2l+j+1)!}$$

$$\Theta_{lm}(\theta) = 2^{-l-1/2} l! [(2l+1)(l-|m|)!(l+|m|)!]^{1/2} |\sin^{|m|}\theta| \sum_{j=|m|}^l (-1)^{l-j} \frac{(1+\cos\theta)^{j-|m|} (1-\cos\theta)^{l-j}}{j!(l+|m|-j)!(l-j)!(j-|m|)!}$$

$$\Phi_m(\varphi) = (2\pi)^{-1/2} (\cos m\varphi + i \sin m\varphi)$$

This function consists of a function Ψ (psi, pronounced “SIGH”), which is composed of three independent functions: R , Θ , (theta) and Φ (phi). It is Ψ^2 which gives us the probability of finding an electron within a specific area around the proton. See if you can find in this solution the origin of the “rules” for the quantum numbers n , l , and m . For example, how does this solution require that n not be 0? Given a specific value for n , what limitations are put on l ? Given a specific n and l , what limitations are put on m ? [Hint: Take a particularly good look at the factorials.]

Using the computers in Sc 353, run the ORBITAL program, which will allow you to take a closer look at the probability of finding the electron at various places around the proton for specific values of n , l , and m and discover the “meaning” of these quantum numbers. For this part of the experiment, you should take notes in your notebook in the form of sketches of the two types of output the program provides: Information relating to the probability of finding the electron at various distances from the proton and information relating to the probability of finding the electron at various positions around the proton.

Describe the following states in terms of average distance from the radius, *nodes* (places where the probability of finding the electron is zero, both angular and radial), and overall shape.

- | | |
|---------------------------|---|
| a) $n = 1, l = 0, m = 0$ | f) $n = 2, l = 1, m = 1$ |
| b) $n = 1, l = 1, m = 1$ | g) $n = 2, l = 2, m = 1$ |
| c) $n = 2, l = 0, m = 0$ | h) $n = 3, l = 2, m = 1$ |
| d) $n = 2, l = 1, m = -1$ | i) any n of your choice between 4 and 6 |
| e) $n = 2, l = 1, m = 0$ | with appropriate l and m . |

Note that radial nodes will be evident on the radial probability plot within the ORBITAL program when color is used emphasize nodes. These radial nodes are actually spheres around the nucleus where the probability of finding an electron is zero. Angular nodes, on the other hand, will be depicted on the full display as surfaces (planes or cones) slicing through the nucleus at various angles.

Part B Data Analysis

Determine the relationship between the number of nodes (total, radial, and angular) and the quantum numbers n , l , and m ?

Discussion

1. Describe how the lines of the hydrogen emission spectrum you observed arise from hydrogen atoms falling from one state to another. Why can't we see the transitions from level 5 to level 1 or from level 6 to level 3?
2. Compare your determination of the ionization energy of the hydrogen atom, R_H , with that given in your text.
3. Using your value for R_H , predict the wavelength of the *fifth* Balmer line (level 7 to level 2).
4. How would you describe the "meaning" of n ? of l ? of m ?
5. Where exactly in the solution to the Schrödinger Equation would you find the "rules" for n , l , and m ?
6. What is the relationship between the number of nodes (total and of each type) and the quantum numbers n , l , and m , and how is this supported by your observations?
7. Describe in your own words precisely what it would mean for the hydrogen atom to drop from the $n = 2$ level to the $n = 1$ level in terms of probability.


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