

THE EMISSION SPECTRUM OF HYDROGENI. INTRODUCTION

One of the most interesting phenomena in nature is the fact that elemental substances such as sodium, mercury or hydrogen absorb and emit light at only at a number of well-defined frequencies. These atomic absorption and emission spectra, as they are called, became one of the most important tools used to investigate the quantum mechanical nature of matter at the atomic scale. They were the motivation behind the development of the Bohr model of the Hydrogen atom. They continue to be a significant test for the more sophisticated atomic and molecular models used today.

For hydrogen, the spectral lines of a given element can be grouped into series of lines, labeled  $n_s = 1, 2, 3$ , etc., and the lines in each series can be numbered from  $n = n_s + 1$  to  $n = \infty$ . An experimentally derived expression for the wavelength of the spectral line as a function of the number of the line in the series was obtained by Balmer for the visible series in the hydrogen spectrum

$$\frac{1}{\lambda} = R \left( \frac{1}{4} - \frac{1}{n^2} \right),$$

while Rydberg later generalized the Balmer results for all the series for the hydrogen atom

$$\frac{1}{\lambda} = R \left( \frac{1}{n_s^2} - \frac{1}{n^2} \right),$$

where  $R = .0110 \text{ nm}^{-1}$  is the Rydberg constant.

The Bohr model of the atom provided the first insight into the physical meaning of the labels for the spectral lines and the spectral series,  $n$  and  $n_s$ , respectively. It also provides a theoretically determined value of  $R$  that matches the experimentally obtained result. The Bohr model postulates that the electron in orbit around the hydrogen nucleus is allowed to have only certain, well-defined energies. The orbital energies are labeled from  $n = 1$ , which is the ground state, or lowest energy level, up to  $n = \infty$ , which corresponds to a free electron that is not bound to the hydrogen nucleus at all. The electron is allowed to have these energies while in orbit around the nucleus, and

no other. According to Bohr's model, the discretization of the energy levels for the electron in the atom is a direct result of the quantum mechanical nature of its orbital motion about the nucleus.

Assuming that this model is correct, we can explain why hydrogen absorbs light only at certain frequencies, and, when excited, emits light at those same frequencies. As we have shown in Experiment #1, light of frequency  $\nu$  consists of photons, labeled  $\gamma$ , each of which has the energy  $E_\gamma = h\nu$ . Under most circumstances, the electrons can absorb only one photon at a time. If the electron is initially in the state  $n = 1$ , the photon it absorbs must give it an energy corresponding to the energy of the states  $n = 2, 3$ , etc. Otherwise, the photon cannot be absorbed at all. Therefore, the photon energy  $E_\gamma = h\nu$  must be equal to  $\Delta E_{1n}$ , the energy difference between the 1st orbital energy and the  $n$ th orbital energy. And if the electron in the atom is excited to a higher energy level by some means, it will eventually give up its energy as a single photon with energy equal to  $\Delta E_{n_i n_f}$ , the energy difference between the higher energy level,  $n_i$ , and the final energy level,  $n_f$ . The different series of spectral lines correspond to the set of all possible transitions to each of the different final states. For instance, the Balmer series in hydrogen involves all the possible transitions down to the  $n = 2$  orbital state. A massive number of such transitions is responsible for the light we see from the hydrogen and mercury vapor lamps.

In this experiment, we will use a diffraction grating and a spectrometer to resolve the hydrogen light into its visible spectrum, and determine the wavelength of the spectral lines as a function of the initial orbital energy level,  $n_i$ . The visible spectral lines are part of the Balmer series, for which we know that  $n_f = 2$ , and we will plot  $1/\lambda$  vs.  $1/n_i^2$  to verify that this is a linear relationship, and also predict the value of  $R$ , the Rydberg constant. In doing so, we will have indirectly demonstrated the quantum mechanical nature of the electronic behavior in hydrogen. We will also use one of the spectral lines from the mercury vapor lamp of known wavelength (See Exp. #1) to verify the grating spacing guaranteed by the manufacturer.

## II. APPARATUS AND PROCEDURE

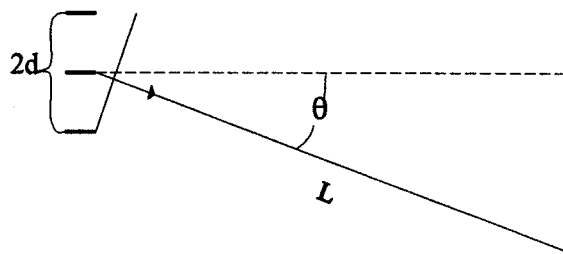
The use of the spectrometer is described in Appendix C at the back of this lab manual. Special care must be taken to reduce as much as possible any extraneous light so that all four visible lines in the hydrogen spectrum can be seen. It is a common mistake to identify the strong blue-violet line as the much weaker violet line. You should increase the slit width in order to observe the violet line. Remember, however, that the wider the slit, the greater the error in determining the diffraction angle. In general, you should use the minimum slit width at which the spectral line can be observed in order to obtain precise and accurate results.

Make sure that the diffraction grating is placed on the center stand so that the light from the telescope is incident normally upon the grating. For normal incidence, the positions of the spectral lines are given by

$$m\lambda = d \sin \theta,$$

where  $m$  is the spectral order,  $\lambda$  is the wavelength of the spectral line,  $d$  is the distance between rulings on the grating, i.e., the "grating constant" and  $\theta$  is the diffraction angle.

**Q.1.** Derive the expression  $m\lambda = d \sin \theta$  for light passing through two slits separated by a distance  $d$  using Fig. 1. Assume that  $d \ll L$ , the distance from the diffraction grating to the point of measurement. As in the Bragg scattering formula, you should calculate the path difference for light passing through the two slits and then impose the condition for when the light will interfere constructively. Note, however, that this formula is not the same as for Bragg scattering. Explain the difference.



**Figure 1.** Sketch for deriving the relationship between the slit spacing and angle of diffraction.

The angle  $\theta$  is measured from the  $m = 0$  spectral line. However, in order to decrease the percentage error of our measurement of the angle, we will measure the angle for the  $m = 1$  spectral line of the same wavelength  $\lambda$  both to the right and to the left of the  $m = 0$  line and take the difference between the two recorded angles. Dividing by 2, we then obtain  $\theta$ , but with an error  $\frac{1}{2}$  as large as if we had measured  $\theta$  from the  $m = 0$  line.

Now measure  $2\theta$  for  $m = 1$  for each of the four visible lines in the spectrum. The short wavelength lines will be closest to the  $m = 0$  line. Calculate the wavelengths of the lines you can see, expressing these to no more significant figures than are justified by the data, and plot  $1/\lambda$  vs.  $1/n_u^2$  (using your experimentally obtained values of  $\theta$ ). What shape curve is expected? Use a table as follows:

Hydrogen line-color	Red	Blue-Green	Blue-Violet	Violet
Grating constant d (Å)				
Reading (deg.)--right				
Reading (deg) --left				
Difference (=2θ) deg.				
θ deg.				
Sin θ				
λ (Å)--experimental				
For graphing: Quantum number n <sub>u</sub>				
1/n <sub>u</sub> <sup>2</sup>				
1/λ <sub>exptl</sub>				

Use the Rydberg equation

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

to show that the y-intercept is R/4. Find R from your graph, then use it (a) to find the short wavelength limit of the Balmer series, and (b) in conjunction with the Rydberg equation and the Einstein relationship

$$E_{\text{photon}} = hc/\lambda$$

to determine E<sub>i</sub>, the ionization energy of hydrogen. In a table, compare the two results with the published values.

### III. DETERMINATION OF THE GRATING CONSTANT

Now, using a line of known wavelength, let's test the information given by the manufacturer about the grating. As a standard for calibrating, use one of the strong lines of mercury (See Exp. # 1). Take first- and second-order readings on both sides of zero-order, and from these determine the grating constant d and the number of grooves per unit width. As usual, express your result to no more significant figures than are justified by your data. Compare your result with that obtained from the manufacturer's value given on the grating. Use a table as follows:

Line-color from mercury spectrum		
$\lambda$ (Å)		
Spectral order m	1	2
Reading (deg.)--right		
Reading (deg) --left		
Difference ( $=2\theta$ ) deg.		
$\theta$ deg.		
Sin $\theta$		
Grating constant d (Å)		
Grating lines per mm (expt)		
Grating lines per mm (manufacturer)		

Make sure that you record the error in your measurements and calculate the error in your experimentally determined value of d.

With due consideration to the uncertainty in your result, does your result agree with that of the manufacturer? If not, what is a likely reason for the difference?

### PRELAB QUESTIONS

Q.1. Q1 in the text.

Q.2. Using your textbook to help you, derive the expression for R using the Bohr model. Explain briefly how the quantum mechanical or "wave" nature of the orbital motion affects the energy of the nth electronic state in hydrogen and creates the discrete energies of transition observed in the emission spectrum of hydrogen.

Q.3. Why can't we see the transitions to the  $n = 1$  ground state?

Q.4. What is the mechanism in the hydrogen lamp which causes the hydrogen molecules to dissociate into atoms and the atomic electrons to be in higher energy orbital states?