THE ISOTOPIC SHIFT IN THE SPECTRA
OF HYDROGEN AND DEUTERIUM:
OBSERVATIONS USING A GRATING SPECTROSCOPE

Introduction

The goals of this experiment are to measure the wavelengths of the Balmer lines of hydrogen, determine Rydberg’s constant, and observe wavelength shift between hydrogen and deuterium in the H$_\alpha$ line. The first part is not particularly difficult but should provide you with some practice in operating the grating spectroscope. The measurement of the isotope splitting is considerably more difficult and will require careful technique to obtain a meaningful result. You will be required to write a formal abstract which would be suitable for submission to a professional organizations (e.g., AIP, AGU, AAS).

Theory

The visible spectrum of hydrogen is characterized by lines at wavelengths $\lambda$ given by Planck’s relation $\Delta E = h\nu = hc/\lambda$, where $h$ is Planck’s constant, $\nu$ is frequency, and $c$ is the speed of light. The energy $\Delta E$ is equal to the difference in energy between the initial and final hydrogen states, $\Delta E = E_i - E_f$. These energies can be found from quantum mechanics by solving the Schrödinger equation in spherical coordinates, using Coulomb’s law for the potential energy (a good discussion is contained in Chapter 4 of Griffiths, Introduction to Quantum Mechanics).

$$E_n = -\frac{m_e e^4}{2\hbar^2(4\pi\epsilon_0)^2 n^2}, \quad n = 1, 2, 3, ... \quad (1)$$

where $m_e$ and $e$ are the electronic mass and charge, respectively, $\hbar = h/2\pi$, and $n$ is termed the principal quantum number. More accurately, one should solve the problem in a relative coordinate system (i.e. $r$ being the relative distance between the proton and electron). In this case the result is the same except that $m_e$ is replaced by the reduced mass for hydrogen,

$$\mu_H = \frac{m_pm_e}{m_p + m_e} \quad (2)$$

where $m_p$ is the mass of the proton. Combining the above relations, we find that the emission lines of hydrogen occur at wavelengths

$$\frac{1}{\lambda} = \frac{\mu He^4}{4\pi\hbar^5 c(4\pi\epsilon_0)^2} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \quad (3)$$
where \( n_f \) and \( n_i \) are the final and initial energy states, respectively. (For emission spectra, obviously \( n_i > n_f \).) The group of lines for which \( n_f = 2 \) and \( n_i = 3, 4, 5, \ldots \) is called the Balmer series. We will want to observe three of these lines: the \( H_\alpha \) red line \( (n_i = 3) \), \( H_\beta \) blue line \( (n_i = 4) \), and \( H_\gamma \) violet line \( (n_i = 5) \). For these lines one could also write the above as

\[
\frac{1}{\lambda} = R \left( \frac{1}{4} - \frac{1}{n_i^2} \right) \tag{4}
\]

where \( R = \mu_H e^4/4\pi\hbar^3c \) is called Rydberg’s constant. Part of the exercise will be to measure the hydrogen line wavelengths and obtain an experimental value for \( R \).

The wavelengths of deuterium emission lines are obtained in the same way, except that the reduced mass is given by

\[
\mu_D = \frac{(m_p + m_n) m_e}{m_p + m_n + m_e} \tag{5}
\]

Since \( m_p \approx m_n \gg m_e \), the deuterium reduced mass differs from the hydrogen reduced mass only by a very small amount. The ratio of wavelengths between two similar lines of hydrogen and deuterium can be found from the reduced masses

\[
\frac{\lambda_H}{\lambda_D} = \frac{\mu_D}{\mu_H} \tag{6}
\]

which is very close to one; thus, the difference between \( \lambda_H \) and \( \lambda_D \) is also very small and will require careful experimental technique to observe clearly.

### Equipment

- Diffraction Grating Spectroscope
- Hg Discharge Lamp
- H-D Discharge Lamp

### Diffraction Gratings: Theory

The spectroscope used for this experiment consists of a slit and collimator, a reflection grating, and a telescope eyepiece. The grating is the primary optical element of the instrument; its characteristics determine the diffracted angles, dispersion, and resolving power of the spectroscope. The gratings we will use consist of a reflective aluminum coating on a finely corrugated substrate. The corrugation involves thousands of equidistant, parallel grooves called rulings. The edge of each ruling acts as a scattering source, similar to the action of multiple slits, and a diffraction pattern is thus associated with the grating.

As shown in Figure 1 below, the distance between successive rulings, \( d \) (often called the
ruling spacing or grating spacing), determines the condition for constructive interference such that the path length between adjacent rays is an integral number of wavelengths:

\[
\text{Path difference} = d(\sin \theta_r - \sin \theta_i) = m\lambda, \quad m = 1, 2, 3, \ldots
\]  

(7)

where \( \lambda \) is wavelength, \( \theta_r \) is the reflected angle, and \( \theta_i \) is the incident angle. Note that both angles are defined with respect to the normal angle with the reflective surface. The order, \( m \), is simply the position of the diffraction maximum with respect to the central maximum (the case of \( m = 0 \), or for reflection gratings \( \sin \theta_r = \sin \theta_i \)).

For a fixed angle of incidence, it is easy to show from the above equation that

\[
\frac{\Delta \theta_r}{\Delta \lambda} = \text{Dispersion} = \frac{m}{d \cos \theta_r}
\]  

(8)

High dispersion is generally a good thing: it allows us to distinguish between two wavelengths that are close to each other. To maximize the dispersion, we try to use gratings with a small grating spacing (small \( d \)), a large angle of reflection (small \( \cos \theta_r \)), and/or work in high orders (large \( m \)).

The line width is given by the angular spread a diffraction maximum,

\[
\Delta \theta_r = \frac{\lambda}{N d \cos \theta_r}
\]  

(9)

where \( N \) is the total number of rulings illuminated on the grating. Note the product \( N d \) in the denominator is the transverse width of the light beam on the grating. Using equations (8) and (9), we can define the resolving power,

\[
R = \frac{\lambda}{\Delta \lambda} = N m
\]  

(10)

\( \Delta \lambda \) is the wavelength difference of two lines that can just be resolved. Resolving power is obviously increased by packing more rulings into the grating, which also increases the dispersion (smaller \( d \)). On the other hand, for a given grating spacing, the full resolving
power is not realized unless the entire surface of the grating is illuminated (maximizing $N$).

**Grating Spectroscopes**

The basic operation of our grating spectroscopes is shown in Figure 2. Light enters the instrument through a slit on the collimating telescope and parallel rays are directed to the reflection grating. Diffracted light from the grating is focus by the eyepiece. The image observed is that of the slit; the wavelength is determined by the grating spacing and geometry according to equation (7). For our purposes, it will be most practical to operate the grating spectroscopes in first order, so $m = 1$ hereafter. Note that we can determine lambda from $\theta_i$ and $\theta_r$, if $d$ is known. Alternatively, we can calibrate the spectroscope (determine $d$) by measuring $\theta_i$ and $\theta_r$ for lines of known wavelength.

To observe the fine structure of the isotope splitting, we must maximize the dispersion of our spectroscopes. This means, according to equation (8), that we have to set $\theta_r$ as large as possible. However, this still will not guarantee that the lines will be resolved. There is another issue, namely that the widths of the lines must be less than their separation. It must be realized that equation (8) holds only for perfectly parallel incident beams on the grating, which can be realized only in the limit of an infinitely narrow slit at the focus of the collimating telescope. In practice, the slit width will be finite (typically 1 mm to 100’s of $\mu$m), so that the width of the line you observe by eye will be determined primarily by the width of your entrance slit. You will need to adjust this to be as narrow as possible while still maintaining enough intensity to identify the line.

To measure angles of incidence and reflection, you must begin with some references. *All angles measured on the spectroscope will be relative to these references.* First, remove the grating and align the eyepiece so that you can see the slit (see Figure 3). Record the angle
reading using the vernier scale. Next rotate the eyepiece by 90° so that it is perpendicular to the collimator. Finally, insert the grating and adjust the center table so that you can see the 0 order reflection of the slit. In this case, the angle of incidence equals the angle of reflection so that both angles must be 45° (Figure 4). Make sure at this point to record the angle reading for the center table; this will allow you to set the angle of incidence to any desired value later on.

**Procedure**

**CAUTION**: The gas discharge tubes use high voltage (thousands of volts) and can be dangerous. Avoid touching either electrode and keep power turned off except when you have checked for safe operation. The tubes can also get quite hot after continuous operation, so watch your fingers.

1. First, you will need to calibrate your spectroscope by determining the ruling spacing of the grating. Use the Hg lamp, and observe the violet, green, and yellow doublet lines for a zero angle of incidence. Look up the wavelengths for these lines in Herzberg or other suitable reference. By plotting \(\sin \theta_r\) vs. \(\lambda\), you should be able to determine \(d\) from the slope. Be extra careful in estimating your uncertainty, either by repeated trials or by goodness of fit to your line.

2. Measure the wavelengths of the Balmer series lines of hydrogen. Use the H-D discharge lamp operated between 60 to 80 V from the Variac transformer. Do not exceed 90 V! As before you may set \(\theta_i = 0\); however, this time use your measured \(d\) and find \(\lambda\) for the violet, blue, and red lines. Plot \(1/\lambda\) vs. \(1/n_i^2\) and determine Rydberg’s constant from the slope. Make sure to quantify your uncertainty. Look up an “accepted” value and compare with yours.

3. Determine the splitting of the \(H_\alpha\) line. You will need to set \(\theta_i\) so that \(\theta_r\) as close to 90° as possible. I suggest you choose a \(\theta_i\) that makes \(\theta_r\) lie between 85°-88°. Record both \(\theta_r\) and \(\Delta \theta_r\) and use equation (8) to find \(\Delta \lambda\). Be sure to take a number of measurements to get a good idea of the random error in your value. How does your result compare with that expected from theory? What is the most significant source of error in your measurement of the isotope splitting?