SPECTRUM OF THE HYDROGEN ATOM

Since the hydrogen atom has only one orbital electron surrounding a nucleus consisting of a single proton, it has a particularly simple spectrum. In this experiment, part of this spectrum will be determined. The observed frequencies of the lines can then be compared with the values predicted by quantum mechanics.

THEORY

When a high-voltage discharge takes place in H₂ gas at low pressures, many molecules are dissociated into atoms by electron impact. These atoms are in excited electronic states. Such H atoms in excited electronic states spontaneously undergo transitions to lower energy electronic states with the emission of radiation. Quantum mechanics gives an expression for the allowed electronic energy levels of an H atom in terms of a single quantum number n;

$$E_n = -(2\pi^2\mu e^4/h^2)(1/n^2) \quad n = 1, 2, 3, \ldots$$  \hspace{1cm} (1)

where $e$ is the charge on the electron and $h$ is Planck's constant. The reduced mass $\mu$ is given in terms of the mass of the electron $m$ and the mass of the proton $M$ by

$$\mu = mM/(m + M)$$  \hspace{1cm} (2)

Owing to spin-orbit coupling and other quantum dynamic effects the energy levels have a small dependence on another quantum number $l$, where $l$ can assume any integral value less than $n$. This energy effect is very small and can be neglected here.

There is no selection rule for $n$; that is, transitions may occur between any of the levels given by Eq. (1). An energy-level diagram for the H atom is given in Fig. 1. Transitions from upper energy levels to lower levels are shown by the vertical lines. These transitions form several series of lines depending on the quantum number of the lower state. Note that the energy levels converge toward a limit as $n \to \infty$. The shaded area above $n = \infty$ indicates a continuum of energy states corresponding to complete separation of the proton and the electron.

We shall be concerned with the Balmer series, the lines of which fall in the visible region of the spectrum. From Eq. (1), it is possible to predict the frequency of a transition from any upper state with quantum number $n_1$ to any lower state with quantum number $n_2$, since

$$\Delta E = E_{n_1} - E_{n_2} = h\nu = h c \tilde{\nu}$$  \hspace{1cm} (3)

where $c$ is the speed of light and $\tilde{\nu}$ is the frequency in units of cm⁻¹ (equal to the reciprocal of the wavelength $\lambda$ in centimeters). Thus,

$$\tilde{\nu} = -(2\pi^2\mu e^4/h^3 c)(1/n_2^2 - 1/n_1^2) = R(1/n_2^2 - 1/n_1^2)$$  \hspace{1cm} (4)

The quantity $R$ is called the Rydberg constant and has the calculated value 109,680 cm⁻¹. For the Balmer series, $n_2 = 2$ and $n_1 = 3, 4, 5, \ldots$ Equation (4) predicts a series of lines which converge to a high-frequency limit at $R/n_2^2$.

METHOD

The frequency (or wavelength) of these Balmer lines can be determined experimentally by comparing the hydrogen spectrum with a reference spectrum for which the wavelengths are known. The iron or mercury spectra are common choices for reference spectra. (Such reference spectral lines must, of course, have been measured absolutely, as by an interferometric technique.) In this experiment, an Hg lamp will be used because the lines of the Hg spectrum can be identified quite easily. In other work the Fe arc is preferable, since there are many more lines.

A variety of spectrographs are in current use for work of this kind; although differing in details they are basically similar. The sources are mounted in such a way that the hydrogen discharge tube will illuminate half of the entrance slit S and the mercury reference lamp will illuminate the
other half. The Hg lamp is off the optical axis of the spectrograph, and a front surfaced mirror (or a 90° prism) is set at 45° to permit an image of this source to be focused on the slit by a lens.

Another lens renders the light from the slit parallel before it passes through the dispersing prism. A camera lens focuses an image of the slit on the photographic plate.

The two common prism materials for use in the visible and near-ultraviolet regions are glass and quartz. Glass is preferable in the visible, since it gives a higher dispersion (and therefore better resolution). For wavelengths shorter than about 3000 to 3500 Å, most glasses absorb light strongly but quartz prisms may be used. Quartz also begins to absorb light below about 1900 Å. Other prism materials (such as fluorite) may be used below 1900 Å, but diffraction gratings are generally used in the far ultraviolet. Since the Balmer lines are more and more closely spaced and have decreasing intensity as the short-wavelength limit is approached, both high resolution and long exposures are needed to observe lines with high n\text{1} values.

**Light Sources:** The best Hg source is a low-pressure mercury lamp that operates from a small ballast transformer. There is intense ultraviolet radiation from such a lamp that is dangerous to the eyes. Therefore a Pyrex glass jacket should be placed over the Hg arc to filter out this ultraviolet radiation.

Many designs for hydrogen discharge tubes are available. A convenient commercial hydrogen source is a Geissler tube made by the Tube Light Engineering Co., New York. In this tube the pressure has been adjusted to give strong Balmer lines (0.1 to 0.5 Torr). In addition, there is always a weak band spectrum due to molecular hydrogen; hydrogen atoms, formed by the electrode discharge, may recombine on the walls to give H\text{2} molecules in excited electronic states which will emit radiation. Such a band spectrum should be so weak that it will not interfere with determining the Balmer lines. The Geissler discharge tube operates from a neon-sign transformer at about 5000 V and 15 mA; it should glow steadily with a bright red color.

**Hg reference spectrum:** The mercury spectrum is available in the CRC Handbook

**EXPERIMENTAL**

Data will be collected using the fluorimeter and a LabView program called fluorimeter.vi that can be found on the desktop of the computer to the left of the fluorimeter.

Turn off the room lights. Turn on the power for the fluorimeter. Turn the sensitivity down as far as it can go. Open the sample chamber door on the fluorimeter and position the mercury lamp so that it illuminates the entrance slit to the detector. Cover the lamp and slit with a dark drop cloth.

Use the middle knob on the side of the drive motor box on the right side of the to set the drive to neutral. Use the bottom knob on the side of the drive motor box to set the emission monochromator to the start wavelength of your scan. This should be the longest wavelength as the drive motor only scans from long to short wavelength. Use the middle knob to set the drive to Emission at a rate of 100 nm/min. Start the fluorimeter program, data collection will begin when the switch on the drive motor is turned to the “ON” position and stop when the drive motor is switched to “OFF”. Adjust the sensitivity so that peaks are observed that have sharp points and not plateaus. If a peak with a flat top is observed lower the sensitivity or position the lamp further from the entrance slit of the detector.

After the mercury spectrum is observed replace the mercury bulb with the hydrogen bulb in the lamp housing. Scan the hydrogen spectrum. Use the mercury spectrum and the values from the CRC to correct the wavelengths of the collected hydrogen spectrum.
CALCULATIONS
Obtain the frequencies of the Balmer lines $\tilde{\nu}$ (in cm$^{-1}$) from the wavelength values $\lambda$ (in nm). Present a table of both $\tilde{\nu}$ and $\lambda$ values together with the value of $n_1$ for each line observed.

Plot $\tilde{\nu}$ against $1/n_1^2$. If the points fall on a straight line, this is a partial confirmation of Eq. (4). From the slope of this line, determine an experimental value of $R$. In all this work, wavelengths in air have been used; these are related to vacuum wavelengths by

$$\lambda_{\text{air}} = \frac{\lambda_{\text{vac}}}{n_{\text{air}}} \quad (5)$$

where $n_{\text{air}}$ is the index of refraction of air which equals 1.00027 at these wavelengths. To obtain a value of $R$ referred to vacuum, one must divide the experimental value by $n_{\text{air}}$. Compare your vacuum value of $R$ with the theoretical value.

DISCUSSION
Show that a typical line in the Lyman series (n$_2$ = 1) lies in the ultraviolet and that a typical line in the Ritz-Paschen series (n$_2$ = 3) lies in the infrared.

Why do the Balmer lines become weaker toward shorter wavelengths? (The first Balmer line at about 6500 Å may appear weak owing to poor detector sensitivity in the red; it is actually the most intense of all the lines.) What are some experimental factors that influence the line width?

REFERENCES