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 often produced 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\(^1,2\) for the allowed electronic energy levels of an H atom in terms of a single quantum number\(^\dagger\) \(n\);

\[
E_n = -\frac{\mu e^4}{8\hbar^2\varepsilon_0^2 n^2}, \quad n = 1, 2, 3, \ldots
\]  

(1)

where \(e\) is the charge on the electron, \(\hbar\) is Planck's constant, and \(\varepsilon_0^2\) is the permittivity of vacuum. The reduced mass \(\mu\) is given in terms of the mass of the electron \(m\) and the mass of the proton \(M\) by

\[
\mu = \frac{mM}{m + M}
\]  

(2)

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

\[\text{FIGURE 1}\]

Electronic energy-level diagram for the hydrogen atom.

\(^\dagger\) Owing to spin–orbit coupling and quantum electrodynamical 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 splitting is very small and can be neglected here.
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

$$\Delta E = E_{n_1} - E_{n_2} = h \nu = h \nu \tilde{\nu}$$

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

$$\nu = \frac{\mu e^4}{8 \hbar^3 c \epsilon_0^2} \left( \frac{1}{n_2^2} - \frac{1}{n_1^2} \right) = \frac{R}{n_2^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

(4)

The quantity $R$ is called the Rydberg constant and has the calculated value $109,677.5805$ cm$^{-1}$ for H. For the Balmer series, $n_2 = 2$ and $n_1 = 3, 4, 5, \ldots$. Equation (4) predicts a series of lines that 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 (see Exp. 41).

A wide variety of spectrometers and spectrographs (instruments that record the spectra on a photographic plate) can be used to study spectra in the visible and near ultraviolet region. A description of such instruments is given in Chapter XVIII, and this material should be read as background for the present experiment. Figure 2 shows a schematic diagram for a typical prism spectrograph, and a brief description will be given here of this instrument. The sources shown in Fig. 2 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-surface mirror $M$ (or a 90$^\circ$ prism) is set at 45$^\circ$ to permit an image of this source to be focused on the slit by lens $L_1$. The lens $L_2$ renders the light from the slit parallel before it passes through the dispersing
prism $P$. A camera lens $L_3$ 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 300 to 350 nm, most glasses absorb light strongly but quartz prisms may be used. Quartz also begins to absorb light below about 190 nm. Other prism materials (such as fluorite) may be used below 190 nm, 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 $n_1$ values.

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, which 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 of hydrogen discharge tubes are available.³ A convenient commercial hydrogen source is a Geissler tube, since the pressure has been adjusted (0.1 to 0.5 Torr) to give strong Balmer lines. 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 H₂ molecules in excited electronic states which will emit radiation. Such a band

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† To align the sources properly, one may open the slit wide and look in at the camera end of the spectrograph. Adjust the source so that it appears in the center of the slit opening. Then close the slit to a narrow opening, and focus the instrument, using the Hg source until the yellow Hg line is well resolved into a doublet sharply focused in the plane of the photographic plate. A ground-glass plate may be placed in the film position and viewed with a small magnifier.
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.** A print of the low-pressure Hg-arc spectrum is shown in Fig. 3. The upper half of the spectrum was strongly exposed in order to bring out the weak lines, and the lower half was exposed only a short time in order to show the strong lines clearly. The wavelengths of these lines in air, see Eq. (5), are given below the spectrum. The spectrum presented in Fig. 3 was made using Kodak 103a-O spectrographic plates; one can also use type 103a-F plates, which are much more sensitive in the long-wavelength end of the visible range.

**EXPERIMENTAL**

Instructions for the operation of the spectrograph or spectrometer to be used will be given in the laboratory. The procedure described below is appropriate for a spectrograph; obvious simplifying changes can be made if a scanning spectrometer with a photomultiplier detector is used.

The placement of the sources and the focus and slit width settings of the spectrograph will be made in advance by the instructor. The sources should be arranged so that one half of the slit is illuminated by the Hg lamp and the other half by the hydrogen discharge tube. A shutter over the slit permits exposures to be made of each source independently without moving the photographic plate. This is important when wavelengths are to be determined by comparison. The photographic plate is placed in a holder that can be raised or lowered to permit several such pairs of spectra to be taken.

The photographic plates are extremely light sensitive. The plate holder must be loaded and unloaded (and developing must be done) in total darkness. The plate should be placed in the holder in such a way that the emulsion side
faces the shutter. The emulsion side can be detected in the dark by moistening a finger and touching the plate lightly near an edge. The emulsion side will feel sticky. Having loaded the holder, turn on the lights and place the holder in position on the spectrograph. Set the plate-holder position close to one end of its traverse. Check to see that the slit is properly illuminated by each source. Instructions for operating the sources will be given. The hydrogen discharge tube operates on high voltage which is possibly lethal; be very careful. Close the shutter over the slit.

Darken the room and open the shutter on the plate holder. Take an exposure with the hydrogen discharge tube and then with the Hg lamp. Each source should be turned off when not in use. Close the shutter over the slit, move the plate holder, and take another pair of exposures with exposure times different from the first set. Repeat this process several times.

After the final pair of exposures, close the shutter on the plate holder and remove the holder from the spectrograph. Turn on the room lights. Set up three developing trays: one with developer, one with water, one with fixer. Set a timer for 3 min. Darken the room and place the plate in developer, emulsion side up; start the timer. Agitate gently and remove after 3 min. Drain over the developer tray, rinse briefly in water, and place in the fixer. Allow to remain in the fixer at least 10 min. Lights may be turned on after about 5 min.

Examine the plate. If for some reason the plate is not usable, start over again but omit any long exposures if time does not permit them. If the plate is satisfactory, rinse it under running water for 20 min and then allow it to drain and dry for several hours (preferably overnight).

**Measurement of spectral lines.** If a comparator is available, mount the plate on the stage, focus on a suitable pair of exposures, and align the plate so that the spectral lines at both ends of the plate are parallel with the cross hair of the microscope. Starting at one end of the plate, move the stage or microscope until a line is under the cross hair and record the position. Continue this process for all lines, both Hg and H atom (disregard the H₂ molecular band spectrum). Always approach a line from the same direction to avoid errors due to backlash in the screw.

If a comparator is not available, a good enlarger may be used instead. Mount the plate in the enlarger, and project the spectra onto a large sheet of white paper mounted on a drafting board. Choose a suitable pair of exposures and mark the positions of all Hg lines and all H-atom lines with a sharp pencil (disregard H₂ molecular band spectrum). Avoid working near the edge of the image, where there may be distortion. Using a centimeter scale, measure the positions of all lines relative to some arbitrary zero position. Indicate which lines are Hg and which H.

Compare your Hg spectrum with that shown in Fig. 3, and assign wavelengths to all Hg lines. Using a least-squares routine and an empirical polynomial \( \lambda = a_0 + a_1 x + a_2 x^2 + \cdots \), fit the variation of the wavelengths \( \lambda \) with the position \( x \) of the Hg lines on the plate. Once this calibration formula
has been established, it is used for interpolation to convert the positions of the H-atom lines into their wavelengths.

**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 \( 1/n_1^2 \) on a large sheet of graph paper. 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

\[
\lambda_{\text{air}} = \frac{\lambda_{\text{vac}}}{n_{\text{air}}}
\]  

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 650 nm may appear weak owing to poor film sensitivity in the red; it is actually the most intense of all the lines.) What are some experimental factors that influence the line width?

**APPARATUS**

Spectrograph or spectrometer; low-pressure mercury lamp (General Electric, Pen-Ray, or Hanovia Division of Engelhard Industries); hydrogen discharge tube (Geissler tube from Klinger Educational Products Corp., Jamaica, NY and others); mounts and power supplies for both sources; front-surface mirror; lens; spectroscopic plates (Kodak 103a-F); three developing trays; developer (Kodak D19); acid fixer; flashlight; timer; darkroom.

Comparator microscope (or enlarger, drawing board, T square and triangle, good centimeter scale).

† The best experimental value of \( R \) for hydrogen using vacuum wavelengths is known with even greater precision than the theoretical value, which is affected by uncertainties in \( c, \hbar, \, \text{and} \, \mu \). The experimental value usually quoted is \( R_e \) (109 737.31534 cm\(^{-1}\)), the extrapolated value for an electron and a nucleus of infinite mass.
REFERENCES


GENERAL READING