4-1 Atomic Spectra

The characteristic radiation emitted by atoms of individual elements in a flame or in a gas excited by an electrical discharge was a subject of vigorous study during the late nineteenth century. When viewed through a spectroscopic principle, this radiation appears as a set of discrete lines, each of a particular color or wavelength; the positions and intensities of the lines are characteristic of the element. The wavelengths of these lines could be determined with great precision, and much effort went into finding and interpreting regularities in the spectra. A major breakthrough was made in 1885 by a Swiss schoolteacher, Johann Balmer, who found that the lines in the visible and near ultraviolet spectrum of hydrogen could be represented by the empirical formula

$$\lambda_n = 364.6 \frac{n^2}{n^2 - 4} \text{ nm}$$

The uniqueness of the line spectra of the elements has enabled astronomers to determine the composition of stars, chemists to identify unknown compounds, and theme parks to have laser shows.
where \( n \) is a variable integer which takes on the values \( n = 3, 4, 5, \ldots \). Figure 4-2a shows the set of spectral lines of hydrogen (now known as the Balmer series) whose wavelengths are given by Balmer's formula. For example, the wavelength of the \( H_\alpha \) line could be found by letting \( n = 3 \) in Equation 4-1 (try it!), and other integers each produced a line that was found in the spectrum. Balmer suggested that his formula might be a special case of a more general expression applicable to the spectra of other elements. Such an expression, found independently by J. R. Rydberg and W. Ritz and thus called the Rydberg-Ritz formula, gives the reciprocal wavelength as

\[
\frac{1}{\lambda_{mn}} = R \left( \frac{1}{m^2} - \frac{1}{n^2} \right) \quad \text{for} \quad n > m
\]

where \( m \) and \( n \) are integers and \( R \), the Rydberg constant, is the same for all series of spectral lines of the same element and varies only slightly, and in a regular way, from element to element. For hydrogen, the value of \( R \) is \( R_H = 1.096776 \times 10^7 \text{ m}^{-1} \). For

Fig. 4-2 (a) Emission line spectrum of hydrogen in the visible and near ultraviolet. The lines appear dark because the spectrum was photographed; hence, the bright lines are exposed (dark) areas on the film. The names of the first five lines are shown, as is the point beyond which no lines appear, \( H_\infty \), called the limit of the series. (b) A portion of the emission spectrum of sodium. The two very close bright lines at 589 nm are the \( D_1 \) and \( D_2 \) lines. They are the principal radiation from sodium street lighting. (c) A portion of the emission spectrum of mercury. (d) Part of the dark line (absorption) spectrum of sodium. While light shining through sodium vapor is absorbed at certain wavelengths, resulting in no exposure of the film at those points. Notice that the line at 259.4 nm is visible here in both the bright and dark line spectra. Note that frequency increases toward the right, wavelength toward the left in the four spectra shown.
very heavy elements, \( R \) approaches the value of \( R_m = 1.097373 \times 10^7 \text{ m}^{-1} \). Such empirical expressions were successful in predicting other spectra, such as other hydrogen lines outside the visible spectrum.

**EXAMPLE 4-1 Hydrogen Spectral Series** The hydrogen Balmer series reciprocal wavelengths are those given by Equation 4-2 with \( m = 2 \) and \( n = 3, 4, 5, \ldots \). For example, the first line of the series, \( \text{H}_\alpha \), would be for \( m = 2, n = 3 \):

\[
\frac{1}{\lambda_{23}} = R \left( \frac{1}{2^2} - \frac{1}{3^2} \right) = \frac{5}{36} R = 1.523 \times 10^6 \text{ m}^{-1}
\]

or

\[
\lambda_{23} = 656.5 \text{ nm}
\]

Other series of hydrogen spectral lines were found for \( m = 1 \) (by Lyman) and \( m = 3 \) (by Paschen). Compute the wavelengths of the first lines of the Lyman and Paschen series.

**Solution**

For the Lyman series \((m = 1)\), the first line is for \( m = 1, n = 2 \).

\[
\frac{1}{\lambda_{12}} = R \left( \frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} R = 8.22 \times 10^6 \text{ m}^{-1}
\]

\[
\lambda_{12} = 121.6 \text{ nm} \quad \text{(in the ultraviolet)}
\]

For the Paschen series \((m = 3)\), the first line is for \( m = 3, n = 4 \):

\[
\frac{1}{\lambda_{34}} = R \left( \frac{1}{3^2} - \frac{1}{4^2} \right) = \frac{7}{144} R = 5.332 \times 10^5 \text{ m}^{-1}
\]

\[
\lambda_{34} = 1876 \text{ nm} \quad \text{(in the infrared)}
\]

All of the lines predicted by the Rydberg-Ritz formula for the Lyman and Paschen series are found experimentally. Note that no lines are predicted to lie beyond \( \lambda_\infty = 1/R = 91.2 \text{ nm} \) for the Lyman series and \( \lambda_\infty = 9/R = 820.6 \text{ nm} \) for the Paschen series and none are found experimentally.