Experiments involving the spectrum of atomic hydrogen are very useful for introducing the quantization of energy levels (1-3) to chemistry students. Using the Balmer series (4, 5), it turns out that the energy of the lone orbiting electron depends exclusively on the principal quantum number, \( n \). In this case the electron is solely subject to the electrostatic influence of the nucleus. The sodium atom, as any alkali metal, resembles the hydrogen atom in having only one electron in the valence shell. However, the interelectronic interactions must be considered in the energy calculations because of the penetration of this electron into the inner closed shells. As a consequence of the radial probability-density distribution (Fig. 1) the energy levels depend not just on the principal quantum number, but also on the angular momentum quantum number, \( l \). A quantity called the quantum defect, \( \mu \), which accounts for the distinct capability of the valence electrons to penetrate into the atom’s inner closed shells, is usually introduced (5).

On the other hand, many concepts on atomic structure (energy levels, ionization potentials, electronegativity of the elements, and so on) are discussed in terms of effective nuclear charges. In the case of the valence electron of an alkali metal this quantity involves the shielding effect of the inner-shell electrons on the nuclear charge \( Z^+ \) (6-10). The effective nuclear charge depends not only on \( n \) and \( l \) quantum numbers, and can be used to describe the spectral series. It seems to be an easier concept for students to understand than the quantum defect, because it retains the meaning of an integer quantum number, as learned in basic courses. These advantages in using \( Z^+ \) instead of \( \mu \), together with the method presented in this article, overcome the disadvantage that \( \mu \) is practically constant for a given \( l \) (only one value of \( \mu \) has to be calculated for each angular momentum, from the experimental data).

We describe a simple graphical method for using spectral data to determine the effective nuclear charges, \( Z^+_\text{eff} \), felt by the valence electron of sodium in the ground and various excited energy states, the shielding constants \( \sigma_nl \), and the energy levels. The shielding constant represents the amount of nuclear charge screened by the inner electrons on the outer \( nl \) electron, \( \sigma_nl = Z - Z^+_n \, l \), where \( Z \) is the total nuclear charge. This procedure has been used in our undergraduate physical chemistry laboratory classes. Its accuracy is high enough for didactic purposes.

This experiment is very convenient for introducing the concept of angular momentum and its effect on the energies of the orbitals, as well as the concepts of a main subject like spectroscopy.

Methods

The energy term for the sodium atom, \( T_{nl} = R \left( 1/(n - \mu_l)^2 \right) \), corresponds to the binding energy (cm\(^{-1}\)) of an electron in an \( nl \) orbital. Introducing the effective nuclear charge the expression becomes \( T_{nl} = R (Z^+_n)^2/n^2 \). Therefore the Rydberg series (4) for the sodium atom may be rewritten as:

\[
\text{Sharp series} \quad \nu_s = R \left( \frac{(Z^+_n)^2}{n^2} - \left( \frac{Z^+_n}{n^2} \right)^2 \right) \quad n = 4, 5, 6, \ldots \quad (1)
\]

\[
\text{Principal series} \quad \nu_p = R \left( \frac{(Z^+_n)^2}{3^2} - \left( \frac{Z^+_n}{n^2} \right)^2 \right) \quad n = 3, 4, 5, \ldots \quad (2)
\]

\[
\text{Diffuse series} \quad \nu_d = R \left( \frac{(Z^+_n)^2}{3^2} - \left( \frac{Z^+_n}{n^2} \right)^2 \right) \quad n = 3, 4, 5, \ldots \quad (3)
\]

where \( \nu \) are the wavenumbers (cm\(^{-1}\)) corresponding to the transitions between the two terms in the second member.

The effective nuclear charge is a measure of the average nuclear charge felt by the outermost electron in the various orbitals, considering the interelectronic repulsions and its penetration capability. Therefore, effective nuclear charges can be evaluated from experimental data using the eqs 1 to 3. Instead of solving these equations analytically, a graphical approach using spreadsheet software (Origin, Excel, etc.) was employed.

Experimental Procedure

The sodium spectrum can be obtained with any kind of spectrometer, from an old photographic instrument to a modern recording spectrophotometer. The spectrum shown in Figure 2 was obtained with a Jobin Yvon U-1000 instrument that gives the spectrum directly in cm\(^{-1}\). Owing to the exponential variation of the line intensities in a spectral series, the spectrum in the high-energy side was plotted on a logarithmic scale. In the 16,000–18,500 cm\(^{-1}\) region the height of the lines is the intensity (nonlogarithmic) after passing

\[ \text{Penetrating} \quad \text{Non-Penetrating} \]

Figure 1. Radial probability-density distribution (distance in atomic units) for the 3s, 3p, and 3d electrons in the sodium atom. The shaded area corresponds to the core.
through a Corning glass filter #512 (or a neodymium salt solution); this filter reduces drastically the intensity of the yellow line, indicated by (p). The spectrum can be obtained in about half an hour. The calculations and interpretation of the results may take about four hours. The baseline in the high-frequency side shows a structure due to rotational-vibrational bands of Na₂ molecules. This will not be discussed because it is beyond the scope of this article.

Identification of the Spectral Series

The first step in analyzing the emission spectrum is to correctly attribute the spectral series. By a close inspection of the spectrum (Fig. 2), disregarding the fine structure (only the transitions involving the 3P₃/₂ level, in the doublets, will be considered in the following), it is possible to distinguish two progressions of lines, indicated by (a) and (b), which become closer and closer going to higher wavenumbers. Considering eqs 1 to 3, it is evident that when \( n \to \infty \) the sharp and diffuse series tend to the same limit, \( T_{3p} = R(Z_{n*}^2)/3^2 \). Therefore, the two progressions can be attributed to these series.

Assignment of Diffuse Series

The equation for the diffuse series, eq 3, can be written as \( \nu_d = A - BX \), where \( X = 1/n^2 \), \( B = R(Z_{n*}^2) \). From a plot of the wavenumbers (cm⁻¹) as a function of \( 1/n^2 \) for the (a) and (b) progressions only the diffuse series should give a straight line because the d electron is almost nonpenetrating and \( Z_{n*}^2 \) can be assumed as 1. The correct attribution of the principal quantum numbers to the lines can be determined by trial and error, assigning different \( n \) values to the first line in the spectrum (starting with \( n = 3 \)) until the best correlation coefficient is obtained from a linear regression. In this way, the diffuse series can be identified as the progression (a) in Figure 2 and the Rydberg constant and the value of \( T_{3p} \) can be obtained, respectively, from the slope (B) and the linear coefficient (A) of this straight line. We obtained \( R = 110,562 \) cm⁻¹ (lit. 109,734 cm⁻¹ [5]) and \( T_{3p} = 24,489 \) cm⁻¹ (lit. 24,476 cm⁻¹ [11]), as shown in Figure 3.

Assignment of Sharp Series and Calculation of \( Z_{ns}^2 \)

The values of \( (Z_{ns}^2) \) for the ns levels can be determined by substituting the appropriate \( \nu_s \) (beginning with the first of the (b) lines in Fig. 2) and \( n \) values into the expression \( (Z_{ns}^2) = (T_{3p} - \nu_s)n^2/R \). We obtained \( R = 110,562 \) cm⁻¹ and \( T_{3p} = 24,489 \) cm⁻¹ (lit. 24,476 cm⁻¹ [11]), as shown in Figure 3.

Figure 3. Plot of experimental wavenumbers for the diffuse series as a function of \( 1/n^2 \) (filled squares) and the corresponding linear regression (dotted line).

Figure 4. (a): Plot of \( (Z_{ns}^2) \) as a function of \( 1/n^2 \) with the \( (Z_{ns}^2) \) calculated from the spectral values of the sharp series (filled squares) and the corresponding linear regression (full line; eq 2). (b): Plot of \( (Z_{ns}^2) \) as a function of \( 1/n^2 \) for the principal series (filled squares) and the corresponding linear regression (full line; eq 3).
From this equation the squared effective nuclear charge can be estimated for any value of \( n \geq 4 \) (see Table 1). The \( T_{3s} \) and \( (Z_{ns})^2 \) values can be determined straightforwardly from the first line of the principal series (yellow line); since \( T_{3p} \) is already known and \( T_{3s} - T_{3p} = 16,978 \) cm\(^{-1}\), we have \( (Z_{ns})^2 = 41,467 \times 3^2/R \).

### Calculation of \( Z_{np}^* \) and the Energy Terms

Unfortunately, only the 3S–3P transition of the principal series is observed in the visible region of the spectrum (indicated by \( p \) in Fig. 2). The remaining transitions have lines in the ultraviolet region and are filtered by the glass tube of the ultraviolet region. As expected, the energies are listed in Table 1, showing their dependence on the angular momentum. Using the Rydberg series (12, 13), the quantum defects can be determined from the linear and angular coefficients in the plot of the wavenumbers of the spectral lines versus \( 1/n^2 \), starting from the diffuse series where the \( \mu \) for d orbitals (nonpenetrating orbit) is nearly equal to zero. Then, the energy terms \( T_{nl} = R/n^2 \), where \( R \) is the Rydberg constant, can be estimated by substituting the appropriate values of \( \mu \) and \( n \) into this expression.

### Literature Cited


### Table 1. Calculated Effective Nuclear Charges and Shielding Factors for the Sodium Valence Electron

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<th>( \sigma_{n} )</th>
<th>( \sigma_{ns} )</th>
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### Table 2. Calculated Energy Terms and Literature Values for the Sodium Atom

| \( n \) | \( T_{nl} \) / cm\(^{-1}\) | \( \delta(\%) \) | \( T_{nl} \) / cm\(^{-1}\) | \( \delta(\%) \) | \( T_{nl} \) / cm\(^{-1}\) | \( \delta(\%) \) |
|---|---|---|---|---|---|
| 3 | 41,467 | 41,450 | 0.04 | 24,443 | 24,476 | 0.13 | 12,285 | 12,277 | 0.06 |
| 4 | 15,673 | 15,710 | 0.23 | 11,248 | 11,177 | 0.67 | 6,916 | 6,901 | 0.15 |
| 5 | 8,270 | 8,249 | 0.25 | 6,457 | 6,407 | 0.78 | 4,422 | 4,413 | 0.20 |
| 6 | 5,079 | 5,077 | 0.04 | 4,205 | 4,152 | 1.27 | 3,071 | 3,062 | 0.29 |
| 7 | 3,437 | 3,438 | 0.03 | 2,965 | 2,908 | 1.97 | 2,256 | 2,249 | 0.31 |
| 8 | 2,486 | 2,481 | 0.20 | 2,208 | 2,151 | 2.65 | 1,727 | 1,721 | 0.41 |
| 9 | 1,885 | 1,875 | 0.51 | 1,711 | 1,655 | 3.38 | 1,365 | 1,359 | 0.44 |
| 10 | 1,480 | 1,467 | 0.92 | 1,367 | 1,312 | 4.19 | 1,106 | 1,100 | 0.54 |

*Relative error.