Spectroscopy of Hydrogenic Atoms

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Introduction

- Fundamental goal: Understand the structure of atoms.
- Historically, atomic structure provided an important test of fundamental theories such as quantum mechanics and quantum electrodynamics.
- Today, we wish to analyze the structure of atoms using spectroscopy.

Theory: Atomic Transitions and Spectral Lines

- A fundamental object of interest when studying the structure of atoms is the *atomic spectrum*.
- Photons are emitted when electrons transition between energy levels in an atom
- These photons are emitted in a discrete spectrum of frequencies.
- The exact spectrum then allows us to deduce the energy levels of the atom.

Theory: Atomic Transitions and Spectral Lines

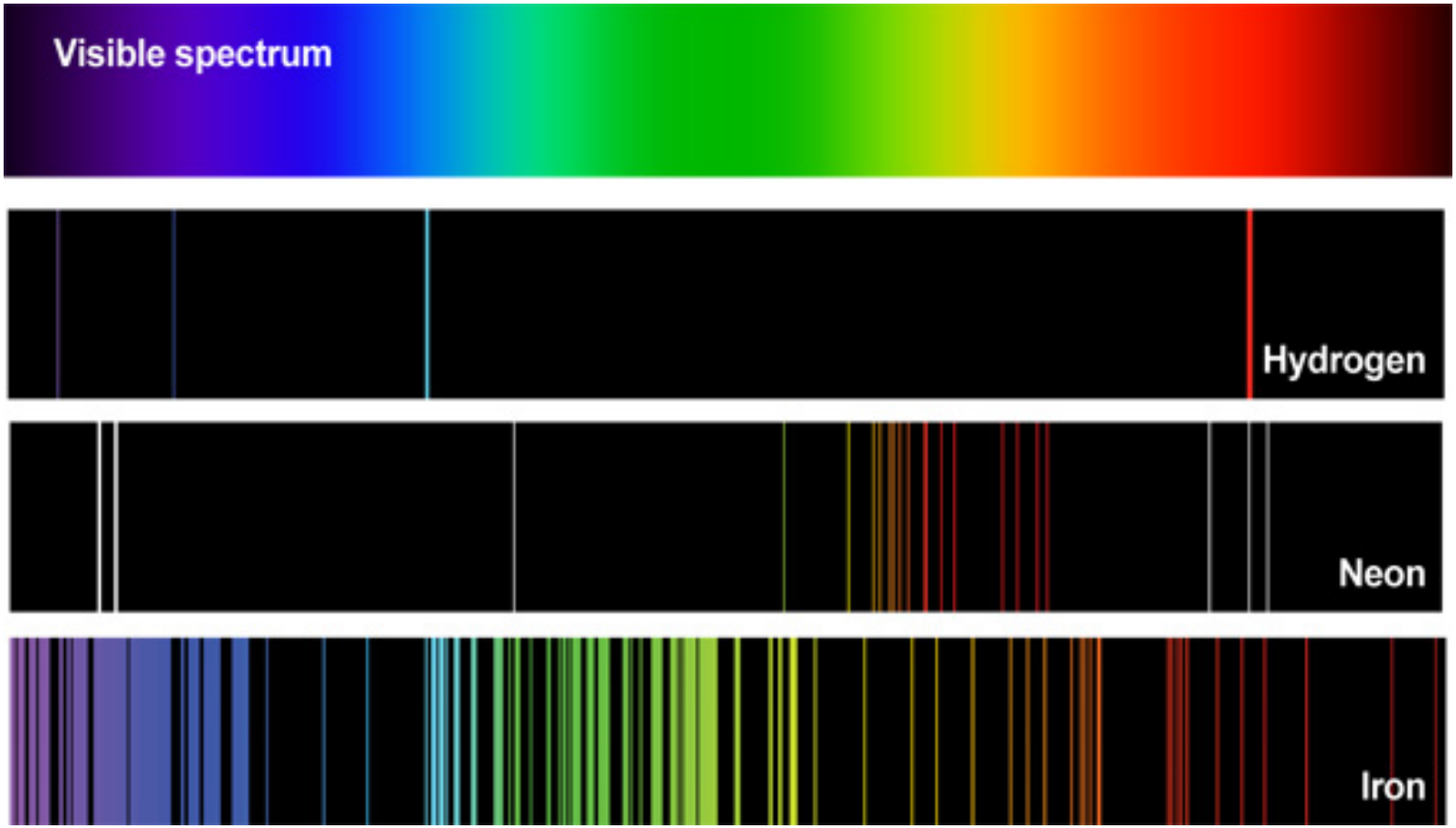

Figure 1: An example diagram showing the visible-light spectrum for various elements (H, Ne, Fe). Note the presence of discrete spectral lines. Source: http://www.ifa.hawaii.edu/newsletters/article.cfm?a=517.

Theory: Hydrogenic atoms and the Rydberg Formula

- Note the complexity of the spectrum of Iron when compared to Hydrogen.
- Iron has many valence electrons, and the electronic transitions between the many bound states for multiple electrons produce a large number of spectral lines, which is often difficult to deal with.
- For simplicity, we will focus on the case of *hydrogen-like atoms* (atoms with a single electron).

Theory: The Rydberg Formula

- From quantum mechanics, there exists a simple formula for the energy of hydrogenic atoms:

$$E_n = E_0 - \frac{hcR}{n^2},$$

where n is an integer (the principal quantum number) and R is a constant depending on the nuclear mass m and atomic number Z:

$$R = \frac{mm_e Z^2 e^4}{8(m+m_e)\varepsilon_0^3 h^3 c}.$$

Theory: The Rydberg Formula

- We then have a corresponding expression for the wavelength of spectral lines:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right),$$

where n_i and n_f are the principal quantum numbers corresponding to the initial and final states of the transition.

Experimental Lines

- In the previous presentation, the spectroscopy of Hydrogen was used to develop a value for the Rydberg constant R_{H} of Hydrogen.
- Here, we will continue to study Hydrogenic spectroscopy to make two additional measurements:
  - Use the shift in spectra between Hydrogen and Deuterium to calculate the mass ratio m_D/m_P
  - Study the spectral line splittings in Sodium

Experimental Line 1: Isotopic Shift and Deuterium

- The Rydberg constant depends on the nuclear mass m and the atomic number Z.
  - For Hydrogen, $Z = 1$ and $m = m_P$
  - For Deuterium, $Z = 1$ and $m = m_D$
- The greater nuclear mass of Deuterium shifts the wavelengths of the spectral lines slightly
- We want to measure this shift to compute m_D/m_P by comparing the $\alpha, \beta, \gamma, \delta$ spectral lines of Deuterium and Hydrogen.

Experimental Line 2: Spectral Line Splitting of Sodium

- We can also consider the spectroscopy of atoms other than Hydrogen.
- Sodium has a single valence electron and the spectral lines of sodium at lower energies arise from transitions between energy levels of this electron.

Experimental Line 2: Spectral Line Splitting of Sodium

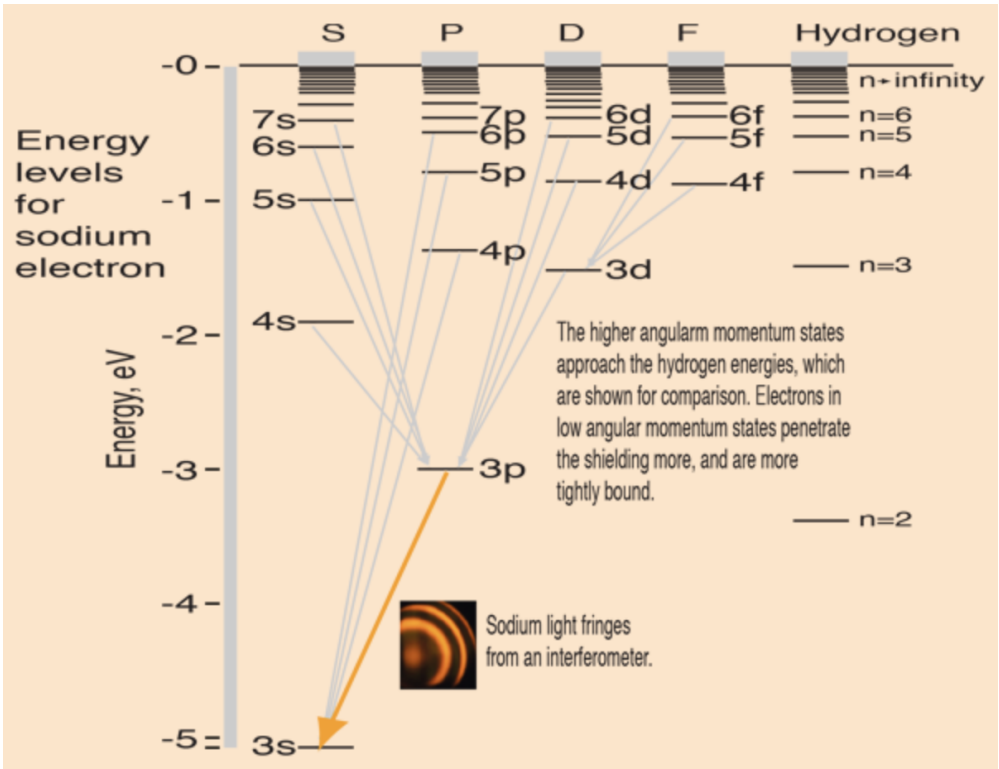

Figure 2: A schematic diagram of the electronic transitions of the valence electron of sodium contributing to the sodium spectrum. Note that the energy levels of sodium are not exactly the same as those of a hydrogenic atom with $Z = 11$ due to screening by the other electrons. Source: [2].

Experimental Line 2: Spectral Line Splitting of Sodium

- The energy level of the ^2P orbitals are split due to spin-orbit coupling (energy of interaction between the electron spin and its orbital angular momentum)
- For transitions involving ^2P orbitals, this results in spectral line *doublets* for sodium.
- We want to identify various sodium lines and measure the spectral line splitting for the ^2P orbitals.

Experimental Methodology: Apparatus

- In order to make our spectroscopy measurements, we used a Jobin Yvon 1250M monochromator to identify spectral lines.
- The wavelengths read by the monochromator differ from the emitted wavelength of the source and require calibration to be accurately read

Experimental Methodology: Procedure

- Calibrate monochromator using the known values of the sharp spectral peaks of mercury.
- Once calibrated, make measurements of hydrogen/deuterium and sodium.
- Use 10 μm slit spacing and 100 ms integration time.

Deuterium Example Data: β-line

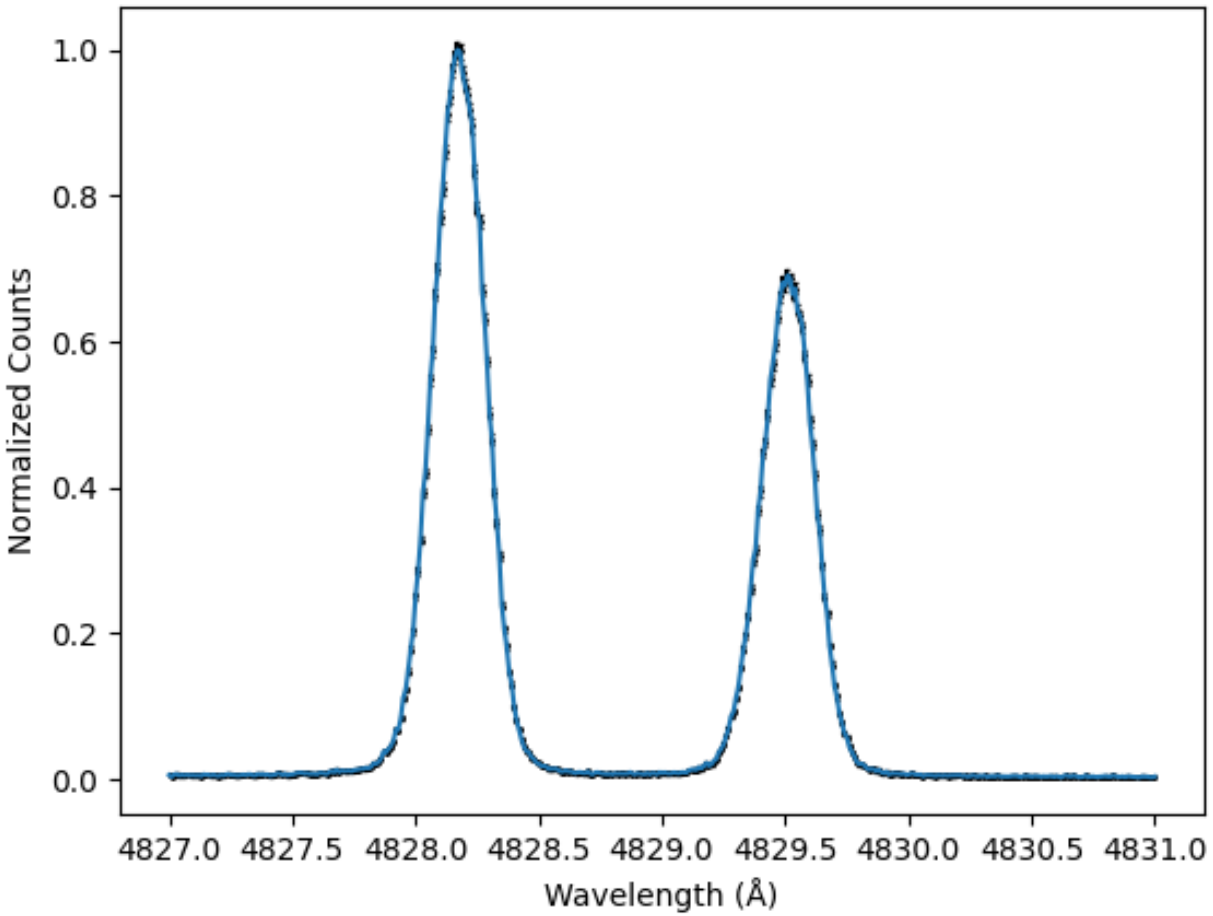

Figure 3: A plot of (normalized) intensity as a function of wavelength in the wavelength range of the expected β-peak of Deuterium and Hydrogen. Note that both the peaks corresponding to Hydrogen and the peak corresponding to Deuterium are observed, with the Deuterium peak being stronger.

Analysis and Uncertainties

- Gaussian fit to peaks yielded χ^2 probability of zero!
- Peaks are not well described by a gaussian, *nor should we need them to be*!
- Compute peak location and estimate uncertainty instead by choosing the local maxima in the graph and finding the furthest points away from local maxima that are within 3σ of the maximum value (~ 0.02 Å)
- Additional contribution to uncertainty
  - Statistical uncertainty in peak location (calculated over multiple measurements within a calibration run)
  - Uncertainty in the calibration slope fit (small)

Results: Mass ratio m_D/m_P

Table 1: The values of m_D/m_P computed from measurements of several different spectral lines of Deuterium and Hydrogen.

Hydrogen/Deuterium Line	Value of m_D/m_P Computed
β	2.04 ± 0.06
γ	2.07 ± 0.09
δ	2.00 ± 0.09

The computed values all agree within uncertainty with the literature value of $m_D/m_P = 1.999$.

Sodium Example Data: D-line

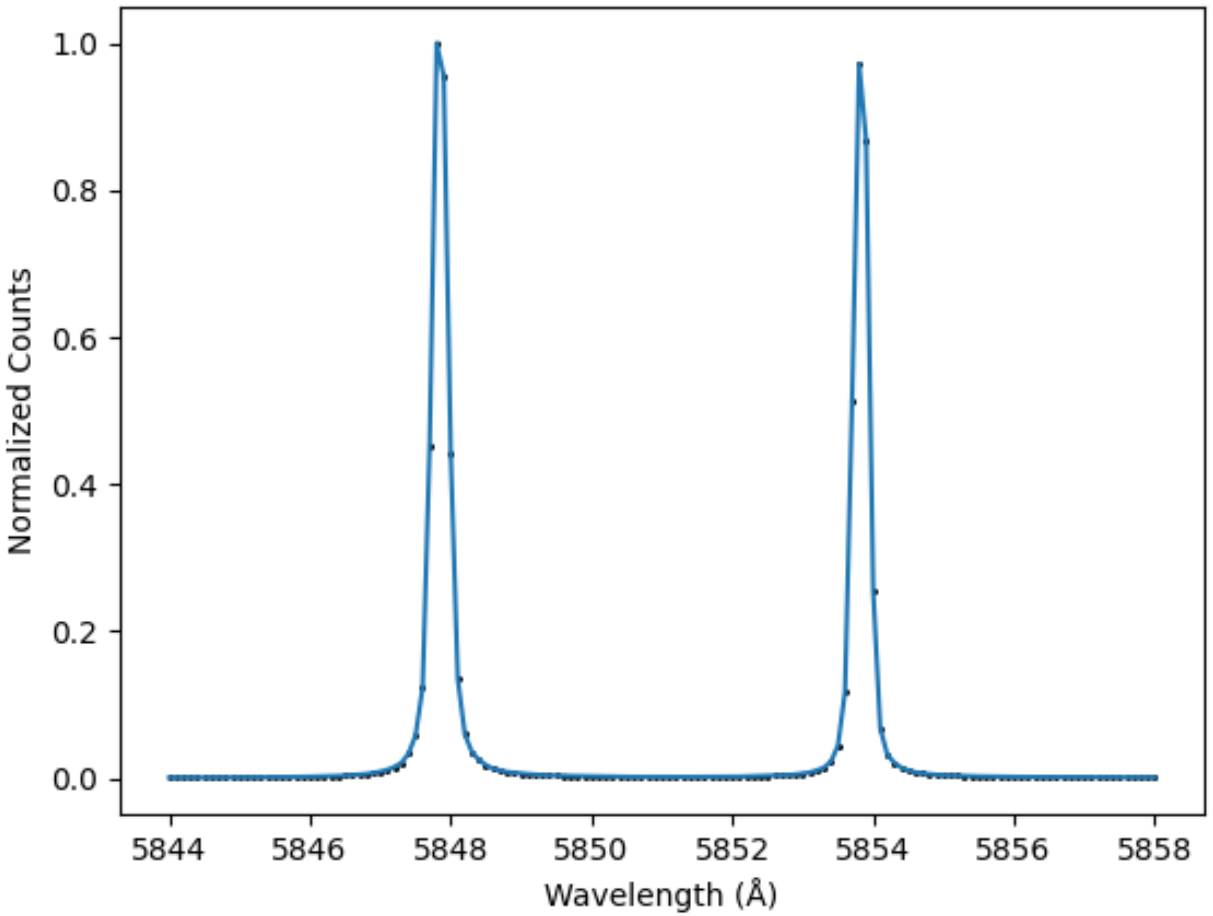

Figure 4: A plot of the (normalized) intensity as a function of wavelength in the wavelength range 584.4 nm $\leq \lambda \leq$ 585.8 nm. Note the two sharp peaks corresponding to a Sodium doublet.

Sodium Example Data: D-line

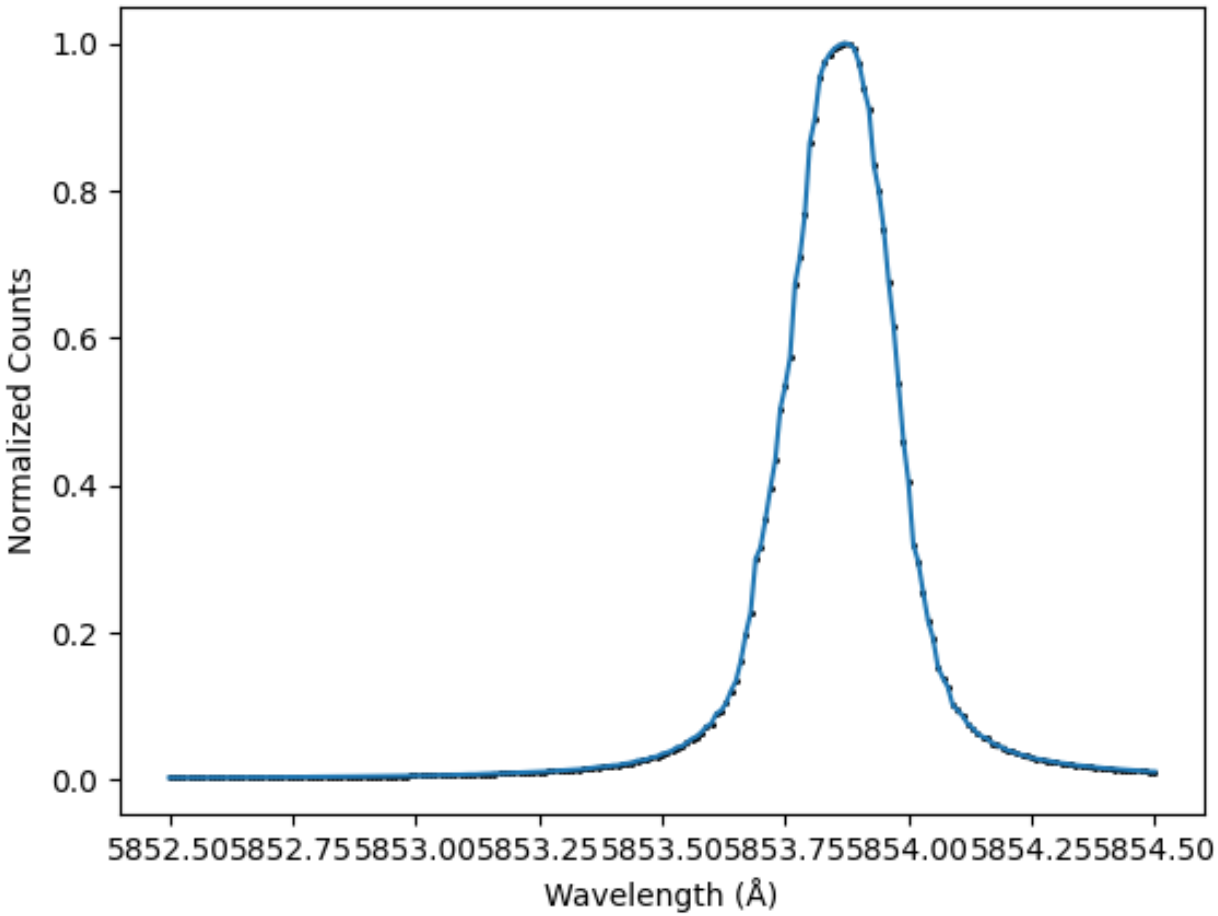

Figure 5: A plot of the (normalized) intensity as a function of wavelength in the wavelength range 585.25 nm $\leq \lambda \leq$ 585.45 nm, which features a single peak of the sodium doublet shown in Fig. 4.

Analysis and Uncertainties

- Note that the sodium peaks are *very* clearly not Gaussian.
- We found the maxima of the sodium peaks using a very similar method to the Hydrogen/Deuterium analysis
- Uncertainty in finding peak location, calibration fit parameters, and statistical variation between measurements

Results: Sodium Spectral Lines

Table 2: Observed sodium doublets with high and low wavelength peak values recorded.

Doublet	λ_{low} (Å)	λ_{high} (Å)
Red	6154.21 ± 0.07	6160.75 ± 0.07
D-Line (Yellow)	5890.00 ± 0.07	5896.06 ± 0.07
Green	5682.55 ± 0.08	5688.17 ± 0.08
Blue	4747.95 ± 0.08	4751.81 ± 0.08
Blue-Violet	4494.29 ± 0.15	4497.76 ± 0.18

Results: Identifying Sodium Lines

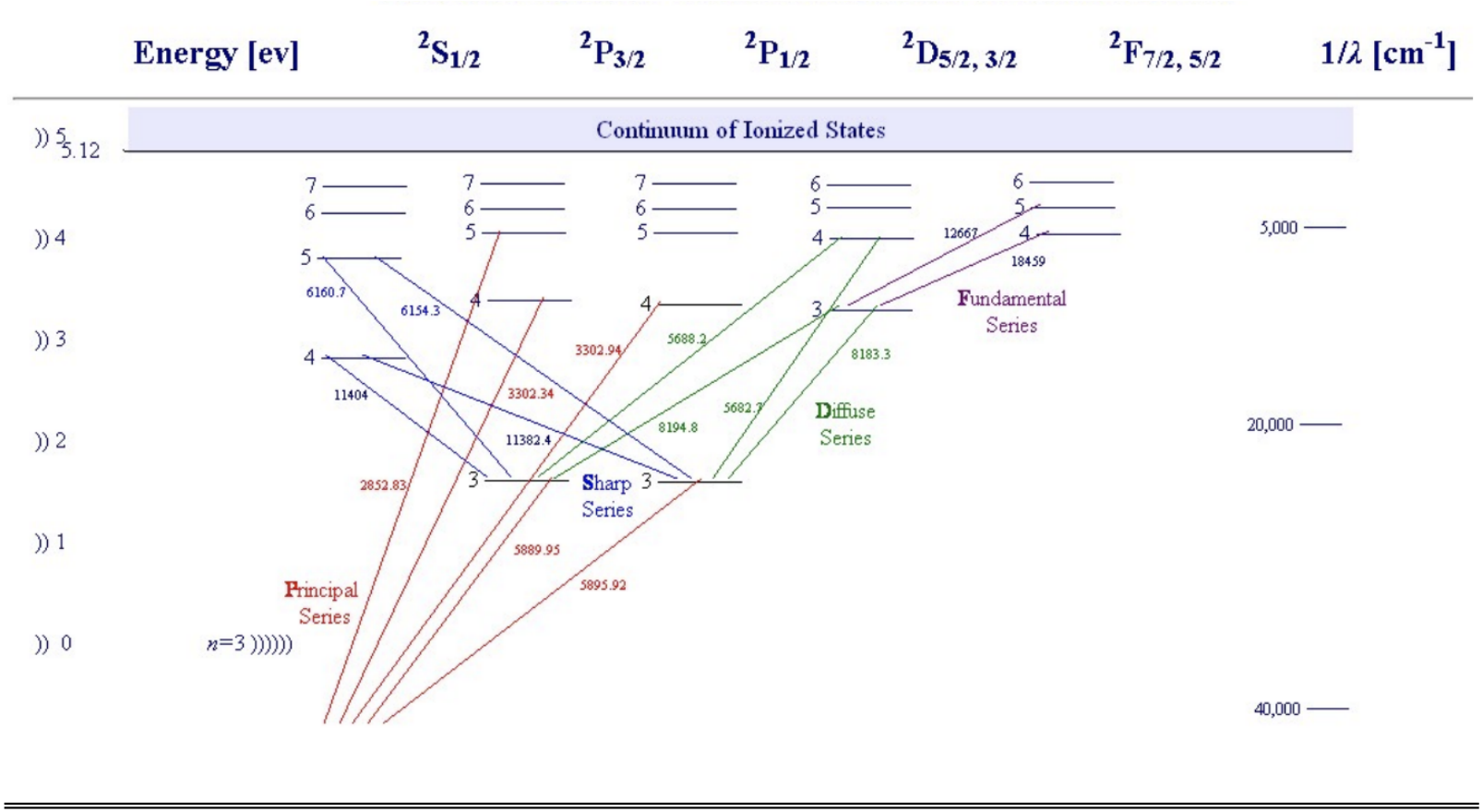

Figure 6: A diagram showing the wavelengths of some of the sodium lines. An extensive analysis using this diagram and other sources was used to determine which observed doublet corresponded to which energy transition. Source: [2].

Results: Identifying Sodium Lines

- We can identify all of the observed sodium lines by carefully inspecting the energy levels of sodium and the observed transition wavelengths:
  - Red: $5S \rightarrow 3P$
  - D-Line: $3P \rightarrow 3S$
  - Green: $4D \rightarrow 3P$
  - Blue: $7S \rightarrow 3P$
  - Blue-Violet: $7D \rightarrow 3P$

Results: Sodium Doublet Splitting

- The doublet splitting for sodium is proportional to $1/\lambda_{\text{low}} - 1/\lambda_{\text{high}}$.
- Since all of the observed sodium lines involve the splitting of the $3P$ level, we should expect the splitting to be the same size for all of our measurements.

Results: Sodium Doublet Splitting

Table 3: Energy splittings corresponding observed sodium doublets.

Doublet	$1/\lambda_{\text{low}} - 1/\lambda_{\text{high}}$ (Å^{-1})
Red	$(1.73 \pm 0.01) \times 10^{-7}$
D-Line (Yellow)	$(1.75 \pm 0.01) \times 10^{-7}$
Green	$(1.74 \pm 0.01) \times 10^{-7}$
Blue	$(1.71 \pm 0.02) \times 10^{-7}$
Blue-Violet	$(1.72 \pm 0.07) \times 10^{-7}$

The computed energy splittings all agree within uncertainty with each other.

Discussion

- Atomic spectroscopy allowed us to deduce fundamental statements about the atomic structure of hydrogen/deuterium as well as sodium.
- In the future, we can further utilize our monochromator to study additional properties.
- Calculate more sodium lines and investigate higher-order splittings