

Atomic and Molecular Spectroscopy

Abstract

We used the hydrogen spectrum to test the Balmer hypothesis. We also derived the Rydberg constant from this information. The sodium spectrum is dominated by the behavior of its single valence electron. We analyzed the sodium spectrum for evidence of nuclear screening and electron spin. Finally, we measured the spectrum of diatomic nitrogen to learn about the chemical bond. The additional degrees of freedom in diatomic nitrogen allow for vibrational and rotational motion.

Introduction

Atomic and molecular spectroscopy has provided experimental verification for many of the most profound predictions in physics. There has been excellent agreement between theory and experiment in the study of visible light emissions.

In this experiment, we used spectroscopy to test theoretical predictions on three levels of complexity. We start with hydrogen, the simplest atom, to test Bohr’s model of quantized atomic energy levels. We then increase the complexity by studying sodium, an alkali atom. Sodium displays nuclear screening, electron spin, and selection rules, all predicted by quantum mechanics. Finally, we looked at the vibrational and rotational excitations of diatomic nitrogen to infer the structure of the chemical bond between the two atoms.

Experimental Procedure

We used an Ocean Optics SD2000 fiber spectrometer calibrated with mercury and helium. The spectrometer consists of two gratings: the master, which has a spectral range of 632 nm to 880 nm, and the slave, which has a spectral range of 371 nm to 677 nm. Both gratings are mounted in a crossed Czerny-Turner configuration. The device has a resolution of  $3.57 \times 10^{-7}$  pixels and is therefore able to resolve features such as the sodium doublet, which has a separation of 0.121 pixels. However, the spectrometer is not fit to study the hydrogen Lyman series, which does not lie in the spectral range of the instrument.

The Balmer Series in Hydrogen

The Balmer formula describes the visible spectrum produced by excited hydrogen atoms. In 1889, Rydberg recognized the Balmer formula to be a particular case of a more general expression in which  $n_1 = 2$  and  $R_H$  is the Rydberg constant.

$$\lambda = G \left[ \frac{n^2}{n^2 - 4} \right]$$

**Balmer Formula**  
(G is an empirical constant)

$$\frac{1}{\lambda} = R_H \left[ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

**Rydberg Formula**

In 1913, Bohr revolutionized our view of the atom with his model of atomic quantization. Bohr suggested that orbital energy is fixed at discrete values, as a function of a quantum number n. Changes in energy states are accounted for by the emission or absorption of a photon, which balances the energy difference.

This relation is described by the Planck formula:

$$\Delta E = h\nu = \frac{hc}{\lambda} = E_2 - E_1 = - \left( \frac{me^4}{2(4\pi\epsilon_0)^2 \hbar^2} \right) \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Our measurement of the visible part of the hydrogen spectrum is evidence of Bohr’s quantized energy levels.

Table 1: Hydrogen Balmer Wavelengths

Measured*	Expected	Transition
656.94 nm	656.28 nm	H <sub>α</sub>
486.07 nm	486.13 nm	H <sub>β</sub>
434.13 nm	434.05 nm	H <sub>γ</sub>
410.28 nm	410.17 nm	H <sub>δ</sub>

\*± 0.1 nm

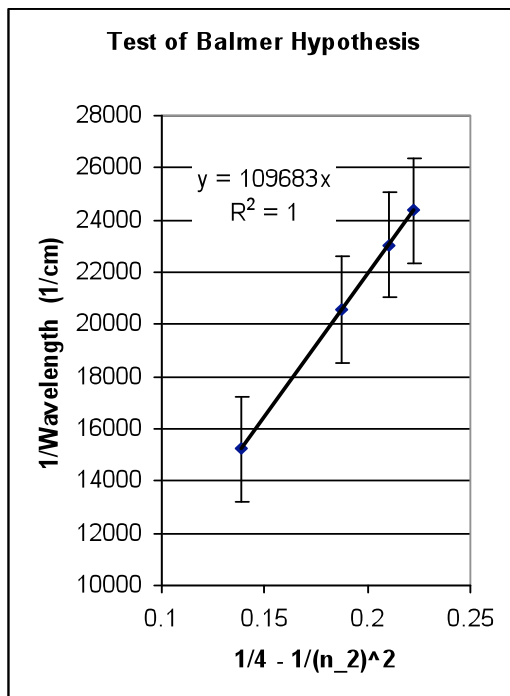


Fig. 1

Figure 1 shows a plot of:

$$\frac{1}{\lambda} \text{ vs. } \left[ \frac{1}{4} - \frac{1}{n_2^2} \right]$$

By the Rydberg formula, the slope of the line gives the Rydberg constant. Our estimation of this constant is  $109683 \pm 1000 \text{ cm}^{-1}$  (accepted value  $R_H = 109737.318 \pm 0.012 \text{ cm}^{-1}$ ).

The straightness of the line is a test of Balmer's hypothesis regarding the quantized energy levels of the hydrogen spectrum. We used Excel to plot a linear trend, which gave an  $R^2$  value of 1. This indicates that a straight line is a good fit for the data, thus verifying the Balmer hypothesis.

### Fine Structure in Sodium

Sodium is an alkali atom, meaning it has one  $l = 0$  electron in its valence shell. As the nucleus is shielded by the charge distribution of the inner shells, this lone electron "sees" a net potential similar to that of hydrogen. However, for smaller  $n$ , the behavior of electrons of small  $l$  deviates from hydrogenic behavior. The small  $l$  states do not have enough angular momentum to maintain a large radius, causing their orbits to cross inside the closed shells (Fig. 2). When this

occurs, there is less of a screening effect and a lowering of the Coulomb energy.

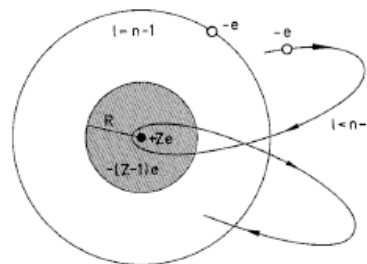


Fig. 2

Evidence for nuclear screening is found by fitting our measurement of the sodium spectrum to a Balmer-like relation. We did this using a quantum defect, which mathematically summarizes the effect of nuclear screening. The quantum defect ( $\delta$ ) is a correction to the quantized energy predicted by Bohr.

$$E_n = -\frac{hcR_H}{(n - \delta)^2}$$

### Bohr energy with quantum defect

Following the selection rule,  $\Delta l = \pm 1$ , the wavelength of a photon emitted to bring an electron from energy state  $nd$  to  $3p$  is determined by:

$$\frac{hc}{\lambda} = E_{nd} - E_{3p}$$

$$\frac{1}{\lambda} = \frac{R_H}{(3 - \delta)^2} - \frac{R_H}{n^2}$$

Figure 3 is a plot of  $1/\lambda$  vs.  $1/n^2$  for transitions from  $nd$  to  $3p$ . The quantum defect calculated from this plot is  $\delta_p = 0.92$ .

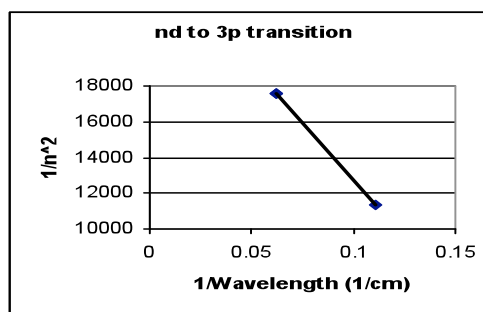


Fig. 3

The sodium spectrum also shows evidence of electron spin. In the rest frame of the electron, the proton creates a circular positive current and therefore produces a magnetic field. The spin of an electron can point either up or down with respect to the internal magnetic field. The interaction energy between the magnetic field and the internal magnetic moment of the electron is described as the spin-orbit interaction.

$$\Delta E = -\frac{g_s \mu_B}{2\hbar} \mathbf{S} \cdot \mathbf{B}$$

$$\Delta E = -\frac{g_s \mu_B}{2emc^2 \hbar} \frac{1}{r} \frac{dV(r)}{dr} \mathbf{S} \cdot \mathbf{B}$$

Since spin can only have two values, the spin-orbit interaction energy can also only have two values:

$$\Delta E = -\frac{g_s \mu_B m_s}{2} B$$

$$= \pm \frac{g_s \mu_B}{4} B$$

The interaction energy is either added or subtracted from the total energy of each state. This leads to a small energy split for every state with  $l > 0$ .

The spin-orbit interaction manifests itself as a  $\sim 0.1\%$  split of spectral lines. Therefore, the presence of doublets in the sodium spectrum verifies the prediction of spin-orbit coupling. These doublets can also be used to infer the magnitude of the internal magnetic field of the atom. The classic example of a doublet is the sodium D line, shown in Figure 4.

We calculated the expected internal atomic magnetic field to be  $1.332 \times 10^{21}$  T for an expected energy split of 0.00617 eV. Our measured energy split was  $0.00104 \pm 0.001$  eV. This gives  $2.2432620 \times 10^{20}$  T for the internal magnetic field, which is about an order of magnitude lower than expected.

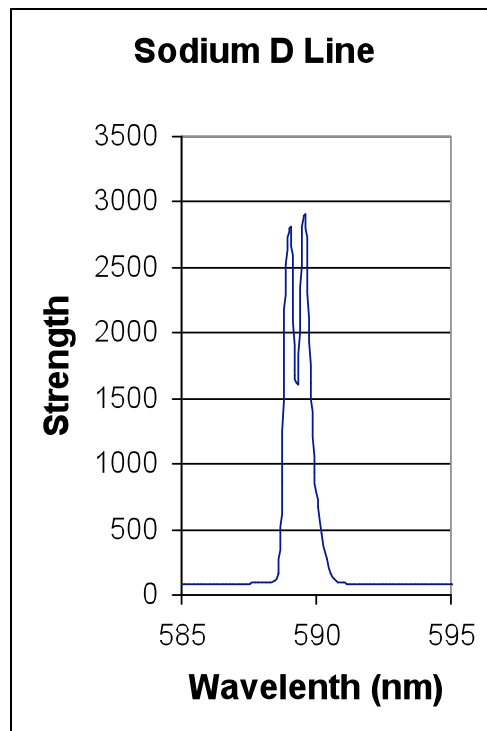


Fig. 4: Sodium D doublet

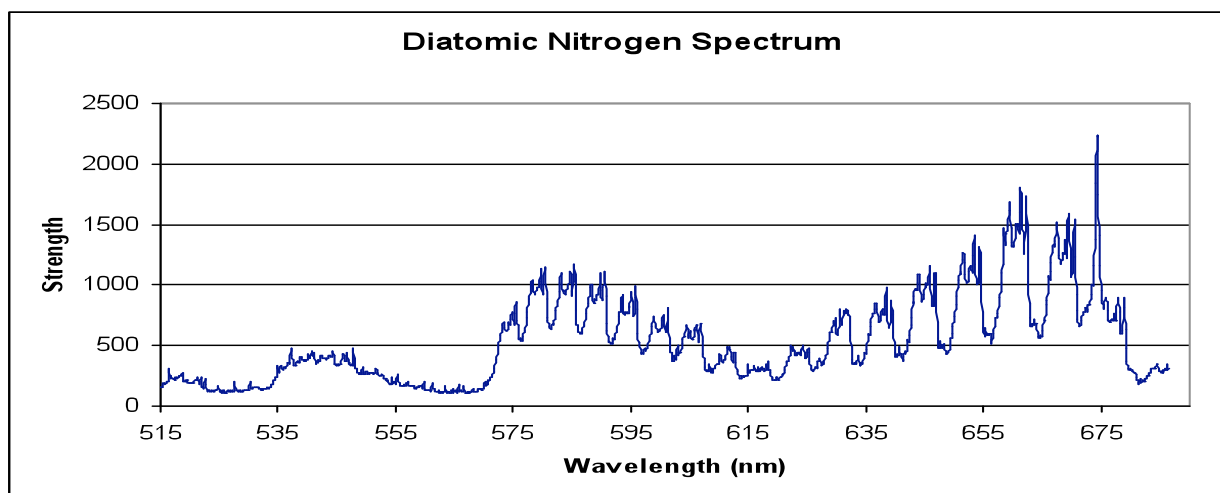
### Molecular Spectroscopy of N<sub>2</sub>

The spectrum of diatomic nitrogen differs from those of hydrogen and sodium greatly. The hydrogen and sodium spectra consist of several sharp peaks whereas the N<sub>2</sub> spectrum shows a broad “comb-like” band of emission wavelengths. Diatomic nitrogen is more complex and has both vibrational and rotational degrees of freedom.

According to the Born-Oppenheimer approximation, vibrational and rotational excitations can be treated separately. The vibrational mode is described by the quantum harmonic oscillator model. In the following equation,  $\omega_0$  represents the fundamental frequency oscillation.

$$E_n = \hbar \omega_0 \left(n + \frac{1}{2}\right)$$

A transition in which  $n$  is decreased by 1 forms a spectrum of equally spaced lines. The separation of these lines can be measured and then used to calculate  $\omega_0$ . In figure 5, the coarser set of lines represents the vibrational excitations. These lines were not exactly equally spaced, which we expect to be the result of coupling with rotational motion. We found the fundamental vibrational frequency of nitrogen to be  $3.11 \times 10^{13}$  Hz.

Fig. 5: N<sub>2</sub> spectrum

The bond holding the two nitrogen atoms together can be viewed as a spring. The strength of the bond can therefore be approximated using  $k=\omega^2m$ , where  $m$  is the reduced mass (7.0015 amu). We found  $k=11.237$  N/m.

The rotational excitations are seen in the fine structure of each of the coarse peaks in the N<sub>2</sub> spectrum. These emissions are described by a quantum rigid rotator.

$$E_{rot} = \frac{h^2 J(J+1)}{8\pi^2 I}$$

In the above equation  $J=0,1,2,\dots$   $h$  is Planck's constant and  $I$  is the moment of inertia of the molecule. For two particles separated a distance  $r$  with a reduced mass  $m$ , the moment of inertia is  $I=mr^2$ .

We again extracted a frequency for rotational motion, which was found to be  $2.52 \times 10^{12}$  Hz. This is an order of magnitude smaller than the vibrational frequency. We also calculated the distance between the atoms as 0.19 nm.

It is curious that the same comb-like structure was not seen in the diatomic hydrogen spectrum. This is because the rotational energy is a function of  $1/m$  and the mass of a hydrogen molecule is very small compared to nitrogen. This would result in emissions with wavelengths much larger than our apparatus can detect.

An application of our knowledge of molecular excitations is found in a common kitchen appliance. A molecule will absorb a photon that matches its fundamental frequency.

This causes the energy of the molecule to increase, which increases the temperature of the material. In a microwave oven, microwaves are used to excite water molecules in order to heat food.

### Conclusions

The atomic and molecular spectra studied in this experiment verify several famous theoretical predictions in physics. The hydrogen spectrum verifies Bohr's model of quantized energy levels. On a more complex level, quantum mechanical predictions of electron spin, nuclear screening and selection rules are manifested in the sodium spectrum. Finally, the spectrum of diatomic nitrogen shows the validity of the Born-Oppenheimer approximation regarding vibrational and rotational energies.

## Appendix

Variables:

- $\lambda$ : wavelength
- $\nu$ : frequency
- $\delta$ : quantum defect
- $R_H$ : Rydberg constant (accepted value:  $109737.318 \pm 0.012 \text{ cm}^{-1}$ )
- $r$ : radial distance from nucleus
- $n$ : principal quantum number
- $l$ : angular momentum quantum number
- $m_s$ : magnetic moment quantum number
- $s$ : spin quantum number ( $s=1/2$  for electrons)
- $h$ : Planck's constant (accepted value:  $4.13566733(10) \times 10^{-15} \text{ eV} \cdot \text{s}$ )
- $\hbar$ : Dirac constant ( $h/2\pi$ ) (accepted value:  $6.58211899(16) \times 10^{-16} \text{ eV} \cdot \text{s}$ )
- $c$ : speed of light (accepted value:  $299,792,458 \text{ m/s}$ )
- $E$ : energy
- $m$ : mass of electron (accepted value:  $9.10938188 \times 10^{-31} \text{ kg}$ )
- $e$ : charge of electron (accepted value:  $1.60217646 \times 10^{-19} \text{ C}$ )
- $\epsilon_0$ : permittivity of free space (accepted value:  $8.8541878176 \times 10^{-12} \text{ F/m}$ )
- $\mu_s$ : magnetic dipole moment
- $\mu_B$ : Bohr magneton (accepted value:  $0.927 \times 10^{-23} \text{ amp-m}^2$ )
- $g_s$ : spin g-factor (for electrons  $\sim 2$ )
- $S$ : spin angular momentum ( $S_z$ : projection of  $S$  on z-axis,  $S_z = \pm \hbar/2$  for electrons)
- $J$ : combined spin ( $J_z$ : projection of  $J$  on z-axis)
- $B$ : magnetic field

Equations referenced:

- Energy of a photon  $\Delta E = \frac{hc}{\lambda}$

- Bohr's orbital energy:

$$E_n = - \left( \frac{me^4}{2(4\pi\epsilon_0)^2 \hbar^2} \right) \frac{1}{n^2}, \text{ with } n = 1, 2, \dots$$

- Spin and Magnetic Moment

$$|S| = \sqrt{s(s+1)} \hbar$$

$$S_z = m_s \hbar, \text{ with } m_s = -s, -s+1, \dots, s-1, s$$

$$S_z = \pm \frac{\hbar}{2}$$

$$\mu_z = -\frac{g_s \mu_B}{\hbar} S$$

$$\mu_B = \frac{e\hbar}{2m} = 0.927 \times 10^{-23} \text{ amp-m}^2$$

$$\Delta E = -\frac{g_s \mu_B}{2\hbar} S \cdot B$$

$$\Delta E \propto \frac{1}{n^3 l(l + \frac{1}{2})(l + 1)}$$

$$\Delta E = -\frac{g_s \mu_B m_s}{2} B$$

$$= \pm \frac{g_s \mu_B}{4} B$$