Ultraviolet Absorption Properties of Diatomic Sulfur

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Ultraviolet Absorption Properties of Diatomic Sulfur

Hannah E. Herde

Submitted in Partial Fulfillment of the Prerequisite for Honors in Physics

Wellesley College

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April 2014
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Chapter 1

Introduction

Successful models of atmospheric physics and chemistry require complete molecular spectroscopic data. Further, interpretations of astronomical spectroscopic observations demand extensive, precise information on atomic and molecular processes. In both cases, the precision of the spectroscopic information strongly affects the veracity of the conclusions.

The work submitted in this thesis contributes to a long term project conducted by Professor Glenn Stark, Wellesley College, and his collaborators to quantify and model photoabsorption cross sections of sulfur-bearing molecules in the ultraviolet (UV). Specifically, this work concentrates on the collection and analysis of diatomic sulfur, S\textsubscript{2}, spectra.

Diatomc sulfur, a rich absorber in the UV from 250-290 nm, is present in atmospheres within our Solar System, particularly those of Jupiter and its volcanic moon, Io (Jessup et al. 2007; Noll et al. 1995; Spencer et al. 2000). Observations of the impact of Comet Shoemaker-Levy 9 with Jupiter in July 1994, as shown in figure [I.1] indicate abundant S\textsubscript{2} in Jupiter’s atmosphere. Unfortunately, the compositions of S\textsubscript{2} on Jupiter and Io remain unknown. Astronomers and planetary scientists are in need of accurate, high resolution spectroscopic information for S\textsubscript{2}, so that they can quantify atmospheric compositions and processes. In particular, they have been thwarted by large uncertainties in the S\textsubscript{2} spectrum.
Figure 1.1: Following the impact of Comet Shoemaker-Levy 9, Jupiter’s stratosphere showed evidence of S$_2$. The y-axis gives the ratio of the pre- and post-impact spectra. [Figure from Noll et al. 1995]

1.1 S$_2$ Thermodynamics

Quantifying the S$_2$ spectrum, by extracting the molecular cross sections, is complicated because it is very difficult to obtain a calibrated S$_2$ spectrum in the laboratory. When heated, elemental sulfur forms a vapor containing molecules with two to eight atoms. These different structural species are called allotropes. The composition of allotropes in the vapor depends on the vapor’s pressure and temperature. In saturated elemental sulfur vapor, high temperatures are necessary for the formation of lighter allotropes at the expense of the heavier allotropes (Steudel & Eckert 2003; Billmers & Smith 1991; Meyer 1976).

---

1‘Allotropes’ refer to different bonded arrangements of atoms. For example, we find carbon atoms bonded together in several different ways, including in a hexagonal lattice (graphite) or a tetrahedral lattice (diamond).
2‘Saturated vapor’ is defined as the equilibrium state of a gas over a liquid at a set temperature in a sealed container.
At low temperatures (<600 K, about 330°C), S\textsubscript{8} accounts for over 90% of the vapor, as reflected in figure 1.2. The composition of heavier allotropes in the vapor steadily decreases as the temperature of the gas rises, until the vapor consists solely of light allotropes - S\textsubscript{2}, S\textsubscript{3}, and S\textsubscript{4}. Above 1000 K (about 730°C), it dominates the vapor’s composition (Meyer 1976). But, as Yomay Shyur ‘11 points out in her thesis, at this temperature, a saturated vapor has a pressure of approximately 76000 torr (100 atm), impractical for laboratory measurements. Fortunately, at constant temperature, the relative composition of S\textsubscript{2} increases as the vapor pressure drops. Meyer reports, “Spectral studies indicate that at 800 K and 100 Torr, S\textsubscript{2} accounts for over 80% of all vapor species. At 1000 K and 1 Torr, the corresponding value is 99%.” Thus, conditions of high temperature and low pressure favor the formation of S\textsubscript{2}, while hindering the creation of other allotropes.

\footnote{100 times the atmospheric pressure on our planet!}


1.2 Experimental Plan

This project uses a two-temperature furnace, designed by Shyur and described in chapter 2 to establish the conditions necessary for $S_2$ formation. The system was tested extensively at Wellesley College before traveling to the National Institute of Standards and Technology (NIST) in Gaithersburg, MD, to make measurements using their Fourier Transform Spectrometer in collaboration with Dr. Gillian Nave. We measured the $S_2$ absorption spectrum from 250-315 nm (about 31,700-40,000 cm$^{-1}$) at a variety of temperatures and pressures over the course of two research trips in December 2013 and January 2014. Chapter 2 describes the experimental design in detail.

This work explores a scheme to indirectly calibrate the $S_2$ photoabsorption spectrum. Despite maximizing the $S_2$ concentrations in the cell, direct calibration of the spectrum remains elusive, since the column density is not accurately known. Existing calculations of vapor composition as a function of temperature fail to provide sufficiently accurate distributions for our purposes. Rather, Professor Stark and Shyur developed a plan to place the spectra on an absolute scale using radiative lifetimes and relative absorption measurements of low vibrational bands. Chapter 3 describes this approach in detail.

1.3 Work in Context

I chose to submit this work for my honors thesis because it encompasses the scientific process. I have experienced multiple phases of the experimental process with this project over several years - including designing and testing the apparatus, making measurements, and performing detail-oriented data analysis. This project continues the thesis work of Yomay Shyur ‘11. I constructed a temperature controller for the two-temperature furnace she designed and tested the system extensively at Wellesley. Professor Stark, Dr. Gillian Nave (NIST), and I completed the high resolution $S_2$ cross-section measurements using the Fourier Transform
Spectrometer at NIST during a three-day trip in January 2014. Chapter 2 describes the experimental design in detail. The theory behind the measurements’ analysis is presented in chapter 3 and the results themselves are presented in chapter 4. Further work includes completing the extensive data analysis of the $S_2$ measurements - ultimately, extracting the cross sections themselves.
Chapter 2

Experiment

This chapter discusses the experimental design for the S\textsubscript{2} cross-section measurements. The first three sections discuss key apparatus - the two-temperature furnace, temperature controller, and NIST Fourier Transform Spectrometer (FTS). The final section discusses the December 2013 and January 2014 experimental runs.

2.1 Two-Temperature Furnace

The vapor in equilibrium above molten elemental sulfur contains allotropes ranging from S\textsubscript{2} to S\textsubscript{8}. A clean spectrum requires a pure sample of S\textsubscript{2} vapor, meaning that the absorption cell conditions must favor S\textsubscript{2} formation at the expense of the other allotropes. As noted in chapter [1] S\textsubscript{2} formation requires conditions of high temperature and low pressure - Meyer predicts that S\textsubscript{2} comprises 99\% of the vapor at 1000 K (about 730\(^{\circ}\)C) and 1 Torr.

Simultaneous high-temperature and low-pressure conditions are not possible using a single-temperature furnace. However, they can be established using a two-temperature furnace. In a single-temperature furnace, the system temperature determines the fixed saturated vapor pressure. In a two-temperature furnace, we can independently set the temperature and
pressure (Shyur 2011). Figure 2.1 depicts the 2.54-cm diameter quartz absorption cell with 10.2-cm side arm prior to its installation in the furnace. The temperature of the side-arm reservoir containing elemental sulfur determines the cell vapor pressure. Meanwhile, the gas temperature is independently controlled by heating the absorption cell to a higher temperature.

Billmers & Smith successfully used a two-temperature furnace to observe $S_3$ and $S_4$. Yomay Shyur ‘11, following their approach, designed the $S_2$ furnace system. She discusses it at length in Chapter 3 of her thesis. The furnace unit as a whole (figure 2.2(a)) creates the desired high-temperature/low-pressure conditions. It consists of a steel conduction block around the absorption cell and a separate copper conduction block around the side-arm reservoir. The conduction blocks distribute heat uniformly across their respective domains. Band heaters warm each conduction block separately. Wellesley machinist Larry Knowles refashioned the original furnace structure, designed by George Dikmak, to improve the portability of the system.
(a) Band heaters warm up conduction blocks around the absorption cell and side-arm reservoir. (b) Heavily insulated, the system rests on fire blocks. It emits visible black body radiation at 700°C.

Figure 2.2: $S_2$ Two-Temperature Furnace

The $S_2$ gas temperature is not particularly pivotal, providing it is well known. Two type-K thermocouples monitor the temperature of the absorption cell conduction block, in thermal contact with the quartz absorption cell. The temperature is stable to within 5°C, given the large thermal inertia of the steel conduction block. The temperature of the side-arm reservoir is critical in order to maintain a stable vapor pressure in the cell. Figure 2.3 plots the logarithm of sulfur’s vapor pressure in Torr as a function of temperature in degrees celsius (Meyer 1976). The vapor pressure is sensitive to small changes in temperature, as manifest by the steep nature of the curve between 100 and 200°C.
\[ \log_{10}(P) = 8.244 \log_{10}(T) - 18.718 \]

*Figure 2.3:* Logarithm of Sulfur Vapor Pressure (Torr) vs Temperature (°C), derived from Meyer 1976 table X.

The vapor pressure is a measure of the quantity of gas in the cell. A high vapor pressure may result in saturation in the absorption spectrum and the production of heavier sulfur allotropes. Thus, the vapor pressure must be monitored closely. Since the vapor pressure is determined by the temperature of the side-arm reservoir, a temperature control unit was designed and constructed for the that reservoir.
2.2 Proportional-Integral Temperature Controller

The temperature control unit described below was developed with the guidance of Professor Robbie Berg of Wellesley College. Briefly, a thermistor in thermal contact with an object changes resistance according to the temperature of the object (in this case, the side-arm conduction block). The controller records the thermistor reading to determine the current temperature. The controller then compares that temperature to the desired temperature, or ‘set point,’ and alters the power supplied to the side-arm conduction block band heater accordingly. This section discusses the design and implementation of the controller.

For simplicity, ‘side-arm reservoir conduction block’ will be referred to simply as the ‘side arm’ from this point forward.
2.2.1 Design

Designing an effective and efficient temperature controller requires consideration of several things:

1. What is the desired range of set points? At what temperature(s) should the system operate?

2. How closely must the temperature be controlled? In this case, how consistent must the temperature be in order to minimize fluctuations in vapor pressure?

3. By what means can the measured temperature and the set point be compared?

The answer to the first question depends on the details of the experiment and determines which components will be suitable choices for temperature measurement. For example, most thermometry fails at high temperatures (Moore et al. 2009). Thermocouples, however, remain reliable. Thus, they are an appropriate choice for measuring the absorption cell conduction block temperature, which ranges from room temperature to 700°C. The vapor pressure curve as a function of temperature (figure 2.3) guides our set point selection for the side arm. Low vapor pressure is required for these measurements, so desirable side-arm set points range from 100 to 200°C.

The second question determines the resolution of our controller. In other words, component selection and controller development must take into account the precision required for monitoring the temperature. The design must be optimized for the desired set points and operating conditions.

The third question concerns implementation: what is the most efficient way to achieve and maintain the desired temperature?

The next several sections address these design questions in more detail, dealing with resolution first and culminating in a discussion of implementation.
How much Temperature Control is Necessary?

The goal of this temperature controller is to maintain a consistent vapor pressure in the absorption cell. The relationship between sulfur vapor pressure and temperature, given by equation 2.1, therefore dominates our resolution concerns:

\[ P = (1.914 \times 10^{-19})T^{8.244}, \]  

(2.1)

where \( P \) is the pressure in Torr and \( T \) is the temperature in degrees celsius (Meyer 1976). In order to minimize fluctuations in pressure, changes in temperature must be tightly regulated. Taking the derivative of equation 2.1 with respect to temperature and multiplying both sides by \( \Delta T \) yields the relationship between the change in temperature and the change in vapor pressure:

\[ \Delta P = (1.5770 \times 10^{-18})T^{7.244} \Delta T. \]  

(2.2)

Table 2.1 lists the maximum changes in temperature corresponding to 1%, 5%, and 10% changes in vapor pressure at several set points. Temperature control to within 0.5°C ensures vapor pressure variation no greater than 5%, while control to within 0.15°C maintains the pressure to within 1% over the range of interest. This temperature control unit was designed to control the temperature to within 0.1°C at 170°C.

<table>
<thead>
<tr>
<th>Set Point Temperature (°C)</th>
<th>( \Delta )Temperature (°C) for Specified ( \Delta )Pressure (Torr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1% ( \Delta )Pressure</td>
</tr>
<tr>
<td>120</td>
<td>0.15</td>
</tr>
<tr>
<td>150</td>
<td>0.18</td>
</tr>
<tr>
<td>170</td>
<td>0.21</td>
</tr>
<tr>
<td>200</td>
<td>0.24</td>
</tr>
</tbody>
</table>

*Table 2.1:* Percent changes in pressure as a function of temperature at several set points.
Proportional-Integral (PI) Control

There are several ways to design a temperature controller. The simplest model, called ‘bang-bang’ or ‘on/off’ control, supplies full power to the heating element until the set point is reached. At the set point, the controller cuts the power supply. When the temperature drops below the set point, the controller restores the power supply. Most thermostats, such as those used in our houses, are bang-bang controllers. However, this produces temperature oscillations in excess of 1°C around the set point temperature. A bang-bang controller tends to overshoot the set point, since it supplies full power until reaching the set point. Plus, it lags in reactivating the power supply when the temperature falls below the set point. Proportional-integral (PI) control, also known as ‘two-term’ control, addresses these problems via a feedback mechanism based on the difference between the current temperature and the set point (Moore et al. 2009). Figure 2.5 compares the temperature controller’s performance over 10 minutes using bang-bang or PI control. The oscillation about the set point is clearly visible in the bang-bang control test, while the controller maintains the system at the set point nicely in the PI control test.

The power supplied to the heating element in a PI-controlled circuit is given by:

\[ P = P_B + G(T_s - T) + R \int (T_s - T) \, dt \]  

(2.3)

where \( P \) is the total power, \( P_B \) is the base or background power, \( G \) is the proportional gain, \( T_s \) is the set point, \( T \) is the current temperature, and \( R \) is the reset (or integral) constant. The second term, known as the ‘proportional’ term, provides power to the heater proportional to the difference between the current temperature and the set point. The third term, known as the ‘integral’ or ‘reset’ term, accounts for changes in heat loss to the environment and other factors that change slowly in time. Without this term, the controller may fail to drive the system to the set point. It may not be able to supply enough power to reach...
the set point if it relies solely on the constant and proportional terms in the presence of a persistent environmental obstacle. In other words, under certain conditions, losses to the environment prevent the system from reaching the set point without the additional power bump provided by the integral term. These two additional terms modulate the power as the system approaches the set point, reducing overshoot and maintaining the set point over long times (Moore et al. 2009).

At maximum gain, the system may experience temperature oscillations around the set point, since the power delivered to the heater may not taper appropriately as the system approaches the set point (Moore et al. 2009).
(a) Bang-Bang control results in oscillations around the set point.

(b) PI control maintains the given set point.

*Figure 2.5:* Bang-Bang and PI Controlled Temperature versus time
Component Considerations

A PI temperature controller requires four inputs: the current temperature, the set point, and values for the gain and reset constants. The temperature controller system must measure the current temperature. The other three inputs, depending on the design of the circuit, may be wired into the circuit board or input from computer. The circuitry must compare the current temperature and the set point, and then make decisions about the power supplied to the heating element. For example, a purely analog controller may use operational amplifiers, or ‘op-amps,’ to determine the deviation from the set point and perform the mathematics necessary to modify the power output based on equation 2.3. Its ability to minimize temperature fluctuations depends solely on the physical electrical circuit. A digital controller, using a computer or micro-controller, may make decisions based on the results of computer calculations. Its controlling capacity depends not only on the physical circuit, but also on the software constraints of the computer’s program. The impact of software constraints will be discussed in the context of the S_2 controller.

A major concern in any temperature controller circuit is measuring the system’s current temperature. For S_2, the desired set points range from 100 to 200°C. Fortunately, precise semiconductor thermistors are available with operating temperatures as high as 300°C. Data sheets for thermistors list several important properties:

**Resistance in ohms at 25°C** serves as a reference for thermistor’s resistance at 25°C and is usually the thermistor’s quoted resistance.

**Beta, \(\beta\), the material constant** is the constant in the exponential approximation of the relationship between resistance and temperature. This approximation is based on a simple curve fitting of experimental data. The quoted \(\beta\) value depends on the two temperatures used to calculate it, usually also reported. For example, \(\beta_{25/85}\) is the \(\beta\) value calculated using the measured resistances at 25 and 85°C.
Operating temperature gives the range of temperatures over which the thermistor may operate. Outside the operating temperature range, the thermistor may melt or behave irregularly.

When selecting a thermistor, it is important to consider all of these properties. Otherwise, the thermistor may not report the temperature accurately.

The exponential approximation of the temperature-resistance relationship permits conversion between the measured resistance and the temperature. It is given by:

\[ R = A e^{-\beta/T} \] (2.4)

where \( R \) is the thermistor resistance in ohms at temperature \( T \) in Kelvin, \( A \) is the thermistor resistance at room temperature divided by the exponent’s value at room temperature, and \( \beta \) is the material constant, determined experimentally.\(^2\)

An excellent way to collect a variable resistor reading, like that of a thermistor or potentiometer, is to connect the variable resistor in a voltage divider. A voltage divider splits the input voltage, \( V_{\text{in}} \), between two loads (the two resistors) based on each one’s fraction of the total resistance.

---

output voltage, $V_{out}$, then it is possible to determine the variable resistor’s resistance, $R_2$:

$$R_2 = \frac{R_1 V_{out}}{(V_{in} - V_{out})} \quad (2.5)$$

By comparing the input and output voltages, it is possible to roughly compare the two resistors:

- If $R_2 \gg R_1$, then $V_{out} \approx V_{in}$
- If $R_2 \ll R_1$, then $V_{out} \ll V_{in}$
- If $R_2 \approx R_1$, then $V_{out} \approx \frac{V_{in}}{2}$

These relationships are extremely useful in a laboratory setting. The change in output voltage with respect to $R_2$ is greatest when $R_1=R_2$. However, this limits $V_{out}$ to a maximum of $V_{in}/2$. In order to access a wider range of possible output voltages (and therefore set points, gains, and resets in this case), the maximum resistance of the variable resistor, $R_2$, must be much greater than the resistance of the static resistor, $R_1$. Table 2.2 lists the variable and static resistor combinations used in the $S_2$ temperature controller.

<table>
<thead>
<tr>
<th>Voltage Divider</th>
<th>Variable Resistor</th>
<th>Static Resistor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Side-Arm Temperature</td>
<td>100kΩ thermistor</td>
<td>470Ω</td>
</tr>
<tr>
<td></td>
<td>20kΩ potentiometer</td>
<td>1kΩ</td>
</tr>
<tr>
<td></td>
<td>10kΩ potentiometer</td>
<td>820Ω</td>
</tr>
<tr>
<td></td>
<td>10kΩ potentiometer</td>
<td>820Ω</td>
</tr>
</tbody>
</table>

*Table 2.2: Composition of Voltage Dividers in $S_2$ PI Temperature Controller*

Voltage dividers can be used to provide all the inputs to the temperature controller system. One voltage divider, containing the thermistor, reports the temperature of the system. Three more containing potentiometers allow a user to change the set point, gain, set point, gain, and reset. Typically, one builds a voltage divider so that $R_1$ is the variable resistor. $R_1$ is then given by the familiar equation: $R_1 = R_2 \frac{V_{in}}{V_{out}} - R_2$. In the $S_2$ temperature controller, every variable resistor is in the $R_2$ position. Solving the voltage divider equation, $V_{out} = \frac{R_2}{R_1 + R_2} V_{in}$, for $R_2$ yields equation 2.5.
and reset constants. Both analog and digital systems can process the $V_{out}$ signals in the context of equation 2.3. The next section will discuss implementation of these concepts to create the $S_2$ PI temperature controller.

### 2.2.2 Implementation

The $S_2$ temperature controller is a hybrid, accepting both inputs from a computer connected via a serial port and analog inputs. The unit uses a micro-controller called a LogoChip and software developed in the block coding environment PicoBlocks to interpret the inputs and regulate the power dispensed to the heating element. A voltage regulator maintains a maximum voltage of 3.3 V in the circuitry to protect the LogoChip. The LogoChip controls the power supply to the heating element via a transistor. The controller may be used as a standalone unit or while connected to a computer running the PicoBlocks temperature controller software. Figure 2.4 depicts the prototype controller, built on a breadboard. Figure B.1 in appendix B displays the labelled circuit diagram.

Closer examination of figure B.1 reveals that the LogoChip receives information via its sensor pins from four distinct circuits, each containing a voltage divider, and controls a single circuit via its power pin. The input pins translate the incoming voltage signals between 0 and 3.3 V (the LogoChip’s native voltage) into integers between 0 and 1000, the ‘sensor’ readings in PicoBlocks. In general, an output pin on the LogoChip can be either at high or low voltage, corresponding to on or off. Only the power pin can produce a periodic step function which allows the circuit to be on for a fraction of a period and off for the remainder.

In the $S_2$ temperature controller circuit, the power pin is connected to an n-type metal oxide field effect transistor. A transistor serves as an electronic gate. It has three pins - the gate, source, and drain. Applying a small voltage across the gate electrically connects the drain and source. Thus, a small voltage can safely turn on and off a circuit which delivers
large amounts of power. When a voltage is applied by the power pin across the transistor, the 50 V power supply is connected to the side-arm band heater, allowing the heater to warm up the conduction block. But the current in the heater circuit halts when the voltage across the transistor is removed, corresponding to the off state in the step function generated at the power pin.

Using a coded version of equation 2.3, the PicoBlocks software calculates the power value (between 0 and 10000), based on the four inputs from the voltage dividers (including the current temperature and set point). The power value determines the shape of the power pin’s step function. For example, a power setting in PicoBlocks of 8000 places the power pin at high voltage (on) for four fifths of a period and at low voltage (off) for the remaining fifth of a period. The power pin controls the transistor which governs current flow in the heater circuit. In this way, the power supplied to the band heater is governed by equation 2.3. For example, if the heater power supply is set to 50 V and the power value generated by the software is 5000, then the heater circuit is disconnected for half of the step function’s period. However, the period of the step function is much smaller than the reaction time of the heater circuit, so the band heater perceives an apparent voltage of 25 V.

PicoBlocks

The LogoChip runs programs written in the block language PicoBlocks. By connecting the S₂ circuit to a computer running PicoBlocks via a serial board wired to the LogoChip, one can manually assign the set point, gain, and reset constants, and read the current temperature. PicoBlocks and the LogoChip handle 16-bit integers, up to $2^{16}$ distinct values. They can process integers from -32786 to 32767. This results in computational limits for mathematics in PicoBlocks and on the LogoChip. First, any decimals resulting from a calculation

---

4The current temperature sensor detects a voltage between 0 and 3.3 V and converts that to an integer between 0 and 1000.

5They use the Two’s Complement representation for negative integers.
are discarded. For example, according to PicoBlocks, $10/3 = 3$. Second, if the maximum positive integer, 32767, is exceeded, PicoBlocks misbehaves, producing nonsensical results. Therefore, when programming equation (2.3), the program needed to account for these computational limits. In this implementation, the program staggers the onset of proportional and integral control until the difference between the PicoBlocks sensor readings for the current temperature and set point falls below assigned benchmarks. The benchmarks are calculated based on the gain and reset constants and the computational limit. As a result, high gain and reset constants delay the onset of proportional and integral control by requiring smaller differences between the current temperature and the set point.

**Temperature Conversion**

Equation (2.4) gives the exponential approximation of the resistance of a thermistor as a function of temperature. Using this approximation, information from the thermistor data sheet, and the PicoBlocks sensor number, we can determine the current temperature of the thermistor.

Solving the exponential approximation for the temperature, $T$, in degrees celsius gives

$$T = \frac{\beta}{\ln \left( \frac{R_{\text{therm}}}{A} \right)} - 273.$$  \hspace{1cm} (2.6)

The thermistor is in a voltage divider with a known resistance, $R$, and its resistance is described by equation (2.5). Replacing $R_{\text{therm}}$ in equation (2.6) produces the current temperature as a function of the known resistor’s resistance, two constants of the thermistor ($A$ and $\beta$), and the measured voltages from the voltage divider:

$$T = \frac{\beta}{\ln \left( \frac{R \cdot V_{\text{out}}}{A(V_{\text{in}} - V_{\text{out}})} \right)} - 273.$$ \hspace{1cm} (2.7)

PicoBlocks interprets $V_{\text{out}}$ a fraction of $V_{\text{in}}$, represented as a number, $N$, over 1000 multiplied
\[ V_{in} \]. Plugging this relation into equation 2.7 and doing some algebra reveals,

\[ T = \frac{\beta}{\ln \left( \frac{R\cdot N}{A(1000-N)} \right)} - 273. \tag{2.8} \]

The thermistor used in these experiments was a Honeywell 100kΩ NTC thermistor (Digikey # 480-3135-ND). For this thermistor, \( A = 0.1616 \) and \( \beta = 3974 \)\(^6\) It was paired with a static resistor of \( R = 470 \, \Omega \) in its voltage divider. Therefore, the thermistor temperature in degrees celsius as a function of PicoBlocks number is:

\[ T = \frac{3974}{\ln \left( \frac{(470)\cdot N}{(0.1616)(1000-N)} \right)} - 273. \tag{2.9} \]

Figure C.1 in appendix C plots this thermistor curve. Set points useful in the \( S_2 \) experiments are labeled in the figure.

**Development**

The first prototype of the temperature controller was developed in summer 2012 on a breadboard. As part of PHYS 350: Independent Research in Spring 2013, the prototype was tested extensively to optimize the component choices for the \( S_2 \) measurements. Satisfied with the prototype, the printed circuit board was designed using the freeware, EAGLE Light Edition\(^7\) and submitted to Advanced Circuits\(^8\) for manufacture. In fall 2013, I soldered the components onto the printed circuit board. The completed temperature controller was first used to make \( S_2 \) measurements during a November full system test at Wellesley College in advance of the December trip to NIST. The controller was used with great success on both the December and January runs.

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\(^8\)Advanced Circuits, 21101 E. 32nd Parkway, Aurora, CO 80011. [http://www.4pcb.com/](http://www.4pcb.com/)
Appendix B contains a parts list, schematic, and the controller software, coded using PicoBlocks. Appendix C contains a plot of the temperature reading as a function of PicoBlocks sensor number and a copy of the Python program used to convert the sensor numbers to temperatures in degrees celsius.

2.3 Fourier Transform Spectrometry

This section discusses the instrument used to make the $S_2$ cross section measurements: a Fourier transform spectrometer (FTS). It employs a Michelson interferometer, most famously used to search for the Luminiferous Ether, to measure high resolution spectra with good signal to noise and broad coverage.
Michelson Interferometer

A piece of optics called a beam splitter divides an incoming beam of light into two beams of equal amplitude. Each beam travels along its own path. A mirror reflects each beam along itself back to the beam splitter. Moving one (or sometimes both) of the mirrors varies the length of each arm, altering the path length traveled by the light beams. When the beams return to the beam splitter, it recombines them producing a beam antiparallel and another perpendicular to the original, incoming beam. The interference of the two beams recombined at the beam splitter determines the amplitudes of the resulting antiparallel and perpendicular beams.

Interference defines the process by which two waves, such as the retroreflected beams in the Michelson interferometer, superimpose to form a new wave. The amplitude of the new wave depends on the relative phase difference of the combining waves. In the Michelson interferometer, the two beams begin with the same phase when they are initially divided by the beam splitter. The difference in the distance traveled by each beam as a result of the scanning mirror, called the path length difference, changes the relative phases of the
beams. The maximum path length difference of the scanning Michelson interferometer is $L$.

Waves that are in phase interfere constructively, resulting in large amplitude waves. When monochromatic light is incident on the beam splitter and produces two beams, those beams will interfere constructively when they recombine if the path length difference between the two beams is a multiple of the wavelength of the original beam. In this case, the relative phase between the two beams is zero - they are perfectly in phase.

Out-of-phase waves interfere destructively, producing waves with small or zero amplitude. A path length difference equal to an odd multiple of half of the wavelength of the original beam produces a phase difference of $\pi$ between the beams, making them perfectly out of phase. This results in total destructive interference - there is no resulting propagating wave.

The user records an interferogram, the intensity of the recombined beam as a function of the path length difference produced by the scanning mirror, by placing a detector, such as a photodiode or photomultiplier tube, in the path of the recombined beam. Taking an inverse Fourier transform of the interferogram recovers the spectrum.

**FTS Mathematics**

The amplitude of a monochromatic light beam is the real part of

$$E = E_0 e^{i(\omega t - 2\pi \sigma x)}, \quad (2.10)$$

where $\omega$ is the angular frequency of the light ($\omega = 2\pi \nu$) and $\sigma$ is the wave number of the light ($\sigma = \frac{\nu}{c} = \frac{1}{\lambda}$) in cm$^{-1}$. When two beams of the same wavelength interfere, the resulting beam’s amplitude is the sum of the amplitudes of the interfering beams:

$$E = E_0 e^{i(\omega t - 2\pi \sigma x_1)} + E_0 e^{i(\omega t - 2\pi \sigma x_2)} = E_0 e^{i\omega t} \left( e^{-2i\pi \sigma x_1} + e^{-2i\pi \sigma x_2} \right), \quad (2.11)$$
where \( x_1 \) and \( x_2 \) are the lengths of the paths traveled by beams 1 and 2 along the two optical arms in the Michelson interferometer. The intensity of the resulting beam is the magnitude squared of the amplitude:

\[
B = E^* E = 2E_0^2 [1 + \cos (2\pi \sigma x)],
\]

(2.12)

where \( x = x_2 - x_1 \) is the path length difference. \( 2E_0^2 \) represents the average intensity of the beam. The relative intensities, however, contain the spectroscopic information, so from now on, the average intensity will be ignored.

When making spectroscopic measurements using an FTS, the incoming light is polychromatic, meaning it spans many wavelengths. Summing over all wave numbers gives the intensity of the output:

\[
I(x) = \int_{-\infty}^{\infty} B(\sigma) [1 + \cos (2\pi \sigma x)] d\sigma.
\]

(2.13)

It is mathematically convenient to evaluate the integral from \(-\infty\), even though there are no negative wave numbers. This permits us to take the inverse cosine Fourier transform to recover \( B(\sigma) \):

\[
B(\sigma) = \int_{-\infty}^{\infty} I(x) \cos (2\pi \sigma x) dx.
\]

(2.14)

The function \( B(\sigma) \) is the measured spectrum (Shyur 2011).
Resolution

*Figure 2.9:* Monochromatic interferograms and their measured spectra - the top pair shows an ideal interferogram for monochromatic light, an infinitely long cosine function, and its interferogram, a pure Dirac delta at the input wavelength. The subsequent pairs illustrate the impact of truncating the interferogram on the measured spectrum. A more truncated interferogram corresponds to a wider sinc function, and therefore lower resolution. [Figure from Archer 2012]

The path length of a real scan is not infinite, contrary to the mathematical presentation above. The finite path length difference, \( L \), introduces an instrument function by truncating the interferogram. Ideally, the interferogram of a monochromatic (single-wavelength) light source is an infinite cosine function. The Fourier transform gives the spectrum - a Dirac delta function centered at the input wavelength. Truncating the interferogram reduces the amount of information gathered and thus modifies the outcome of the Fourier transform.
Rather than producing a delta function at the input wavelength, it gives a sinc function centered on the input wavelength. A longer scan allows us to gather more information and subsequently narrow the sinc function. Figure 2.9 depicts the effect of truncating a monochromatic interferogram on its resulting spectrum. The sinc function is called the instrument function:

\[ I = I_0 \frac{\sin(2\pi\sigma L)}{2\pi\sigma L} \equiv I_0 \text{sinc}(2\sigma L). \]  

(2.15)

Figure 2.10 displays an example sinc function.

*Figure 2.10:* Finite path length leads to a sinc instrument function, \( I = I_0 \text{sinc}(2\sigma L) \).

The resolution limit is the distance from the sinc function’s central maximum to the first zero. In a grating spectrometer, the physical number of grooves in the grating determines the maximum resolution. In an FTS, the distance travelled by the scanning mirror(s) sets the maximum optical path length difference, \( L \), between the two beams, and therefore the width of the sinc function (Archer 2012; Shyur 2011; Thorne et al. 1987). The resolution
limit of the FTS in wave numbers is

\[ d\sigma = \frac{1}{2L}. \]  \hspace{1cm} (2.16)

Another way to describe the resolution of a spectrometer is by its **resolving power**,\n
\[ R = \frac{\sigma}{d\sigma}. \]  \hspace{1cm} (2.17)

**Sampling the Interferogram**

The FTS cannot record every point in the interferogram. Rather it samples the signal discretely, recording a data point every minimum sampling interval, \( \Delta x \), required to recover the complete spectrum. This converts the Fourier integrals above to Fourier sums and replicates the spectrum at intervals of \( \frac{1}{\Delta x} \). Mathematically, this corresponds to a Dirac comb of period \( \Delta x \) multiplying the true interferogram. Figure 2.11 illustrates this process.

The Nyquist theorem gives the minimum sampling interval, \( \Delta x \), necessary to resolve the recovered spectrum and prevent overlap of adjacent copies, or **aliases**.

**Nyquist Theorem**: The sampling frequency, \( \frac{1}{\Delta x} \), must be greater than or equal to twice the maximum wavenumber of interest: \( \frac{1}{\Delta x} \geq 2\sigma_{\text{max}} \). Equivalently, the sampling interval, \( \Delta x \), must be less than or equal to the half wavelength of the shortest wavelength of interest:

\[ \Delta x \leq \frac{\lambda_{\text{min}}}{2}. \]  \hspace{1cm} (2.18)

The spacing between two copies, called the **free spectral range**, is \( \Delta\sigma = \frac{1}{2\Delta x} \). 

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Figure 2.11: Discrete sampling of an interferogram - Left: Interferogram (top) multiplies a Dirac comb with period $\Delta x$ (middle) to produce the sampled interferogram (bottom). Right: Fourier transform of the interferogram producing the spectrum (top), the Fourier transform of the Dirac comb (middle), and the Fourier transform of the sampled interferogram producing a series of copies of the spectrum (bottom). Red lines mark out a single spectrum and its copy. [Figure from Blackie 2009]

Choices of detectors and optical filters in the UV typically zero much of the full spectral range $0 - \sigma_{max}$. If the replicas fall outside the measured band pass, we do not risk recovering the replicas. Therefore, we can undersample the interferogram if our data collection is restricted to the free spectral range. Undersampling speeds up data acquisi-
tion. In this work, the spectra were collected in the second alias, meaning that they were undersampled by a factor of 2 - or every $2\Delta x$ (Shyur 2011; Blackie 2009).

**Phase Correction**

An ideal interferogram is symmetric about zero path difference, meaning that $I(-x) = I(x)$. Real interferograms are not perfectly symmetric since the true peak of the interferogram is rarely sampled. A phase correction accounts for this asymmetry (Shyur 2011; Thorne et al. 1987).

Mathematically, when $I(x)$ is symmetric, the complex Fourier transform returns a recovered spectrum, $B(\sigma)$, which is completely real. The recovered spectrum of an asymmetric $I(x)$, $S(\sigma) = \int_{-\infty}^{\infty} I(x)e^{-2i\pi\sigma x}dx$, is complex:

$$S(\sigma) = S_R(\sigma) + S_I(\sigma) = B(\sigma)e^{i\phi(\sigma)}. \quad (2.19)$$

The spectrum in the real domain is given by multiplying $S(\sigma)$ by the phase correction $e^{-i\phi(\sigma)}$:

$$B(\sigma) = \int_{-\infty}^{\infty} I(x)e^{-2i\pi\sigma x}e^{-i\phi(\sigma)}dx. \quad (2.20)$$

The phase, $\phi(\sigma)$, is given by the arctangent of the imaginary part over the real part of the complex spectrum:

$$\phi(\sigma) = \arctan \left( \frac{S_I(\sigma)}{S_R(\sigma)} \right). \quad (2.21)$$

The phase correction is necessary to obtain high resolution spectra in the UV. Dr. Gillian Nave at NIST performs the phase correction as part of the signal processing.
2.3.1 The NIST Fourier Transform Spectrometer

The NIST FT700 FTS was originally designed at Imperial College-London and built by Chelsea Instruments, UK. It was specifically designed to collect laboratory spectra for use in atmospheric and astronomical modeling (Thorne et al. 1987). It was modified at NIST to enhance its performance in the UV. It has a high resolving power, dual output channels, and unique beam splitter. It uses a variant of the standard Michelson interferometer configuration so that no light is reflected back to the source. Designed to function in the far UV, it is suitable for measurements at wavelengths as short as 140 nm (Griesmann et al. 1999).

A 1.5m x 0.25 m x 0.25 m vacuum tank encloses the optics. Inside the tank, carriages hold the catseye retroreflecting mirrors. A linear motor moves the mobile carriage (carrying the scanning mirror) on a ball bearing at constant velocity. The maximum path length difference, \( L \), is 20 cm, giving a resolution limit \( d\sigma = 0.025 \text{ cm}^{-1} \) (equation [2.16]), or a resolving power of \( 2\times10^6 \) at 200 nm (equation [2.17]), making this the world’s highest resolution broadband UV FTS (Griesmann et al. 1999; Thorne et al. 1987).

The catseye mirrors are tilt-invariant, meaning they ensure that an exiting beam is
antiparallel to the incoming beam, regardless of the angle of incidence. Figure 2.12 provides the ray diagram for catseye mirrors. This condition of parallelism is critical because the resolution of an interferometer is severely impacted if the beams are not antiparallel. However, the catseyes cause a lateral displacement in the reflected beams, relative to the incident beams, leading to dispersive optical paths (Thorne et al. 1987). To account for this, a custom-cut plate carved from a single crystal of calcium fluoride (figure 2.13) serves as both a beam splitter and recombiner (Griesmann et al. 1999). Traditionally, interferometers employ an incidence angle of 45° on the beam splitter. This FTS, like its twin in London, sets the beam splitter at 5° to accomplish three things:

1. Reduce vacuum tank volume
2. Maximize surface area use
3. Reduce undesirable polarization in the beam splitter (Thorne et al. 1987)

The catseye mirrors also introduce multiple optical planes (figure 2.14), permitting dual outputs. In a standard FTS, the output of the Michelson interferometer is a beam antiparallel and another perpendicular to the input beam. The input beam, then, obstructs the antiparallel output beam, and therefore, only the perpendicular output beam may be
sampled. The catseye mirrors in the NIST FTS vertically displace the input beam so that the reflected output beam travels in an upper plane. Each output channel, A and B, is collected independently. One can double the number of interferograms recorded at a time, a boon for the signal-to-noise ratio, by collecting the same spectral range at each output. Alternatively, one can collect two spectral ranges simultaneously by using two different detectors (Shyur 2011).

A single-mode, frequency-stabilized helium-neon (HeNe) laser monitors the position of the moving catseye retroreflector by providing a reference light beam. The reference beam follows a path parallel in the middle level to the signal through the FTS. The catseyes introduce horizontal displacement (as opposed to the vertical displacement in the signal) in the laser reflections. The calcium fluoride block has spots to serve as the laser beam splitter and recombiner (figure 2.13). Scanning the mobile mirror produces evenly spaced HeNe interference fringes, which are then used to calculate mirror’s displacement. The laser calibration allows for the calculation of the time as a function of path length difference, \( t(x) \). To obtain \( I(x) \), the interferogram intensity as a function of path length difference, \( t(x) \) is combined with the interferogram intensity as a function of time, \( I(t) \) (Shyur 2011).

Air is highly absorbent in the UV. Therefore, reliable absorption measurements in the UV require a vacuum. The compact vacuum tank not only protects the FTS optics but also permits speedy pump-down to vacuum and minimizes outgassing.

Work in the UV requires greater optical precision. Lenses fail to transmit at short wavelengths and must be replaced by mirrors. The reflectivity of mirrors also declines in the UV. Further, the demand for optical flatness increases. In a two-beam interferometer, the recombining wave fronts must be plane, parallel to one another to within a quarter of the minimum wavelength of interest, \( \lambda_{\text{min}}/4 \), to meet normal requirements for optical flatness.
Figure 2.14: Optical levels in the NIST FTS result from the catseye mirrors. [figure from Blackie 2009]
\( \lambda_{\text{min}} \) in the NIST FTS is approximately 140 nm (the transmission limit of calcium fluoride). Thus, the instrument requires an optical flatness of approximately 35 nm, or about a fifteenth of the wavelength of green light. All optics, including the scanning mirror and beamsplitter, must maintain this wavelength tolerance. The catseyes, in particular, must ensure this tolerance over two times the beam diameter, a consequence of the beam’s horizontal and vertical displacements. Each catseye’s secondary plane mirror must be correctly positioned to within 10 \( \mu \)m (Thorne et al. 1987).

### 2.3.2 Making Measurements

To make a measurement of a gas’ spectrum, an absorption cell filled with a sample is placed between a continuum light source and the FTS. The output light observed by the detectors is unabsorbed light, the rest having been absorbed by the gas in the cell. For broadband absorbers like \( S_2 \), the baseline intensity of the source is irrecoverable from the spectrum. ‘Blank’ scans taken in the absence of gas in the cell are required to establish the background intensity of the light source.

A single scan of the FTS’ mobile mirror over its path length yields a spectrum. A process called **coadding**, however, in which multiple scans are summed together, produces a cleaner signal. Each interferogram has both the desired signal and random noise. By coadding interferograms, we can build up the coherent signal, while the random noise sums incoherently. Thus, we can achieve a higher signal-to-noise ratio (S/N) in the composite interferogram. S/N of a set of \( n \) scans is proportional to \( \sqrt{n} \). Thus, doubling the S/N requires four times as many coadds, and thus unfortunately, increases the measurement time by a factor of four (Shyur 2011).
2.3.3 Detectors: Photomultiplier Tubes (PMTs)

Photomultiplier tubes (PMTs) are best suited for detecting the FTS output signals. They are designed for low-light levels and respond quickly to changes in light intensity. PMTs are often optimized to measure particular spectral ranges.

A PMT contains a photocathode. Each photon incident on the photocathode produces an electron via the photoelectric effect. The electron is then accelerated through an electric field and gains energy. Then, it strikes the surface of a dynode, producing more electrons by secondary emission. Those electrons are accelerated by another electric field to strike a second dynode, producing more electrons and so forth. Thus, a single electron becomes a shower of electrons. The first dynode is at a higher electric potential than the photocathode, and each subsequent dynode is at a higher electrical potential than the previous one, establishing the electric fields which accelerate the electrons. In this way, signal is amplified significantly.

The spectra in this work were collected using two different PMTs, both manufactured by Hamamatsu. Table 2.3 lists their spectral responses, photocathode materials and other important information, recorded from their data sheets. Figures 2.15(b) and 2.15(a) plot the quantum efficiency of each PMT, also reported from their Hamamatsu data sheets. The specific choices for the $S_2$ spectral ranges are discussed in section 2.4.

Table 2.3: Photomultiplier tubes used in $S_2$ cross section measurements at NIST

<table>
<thead>
<tr>
<th>PMT</th>
<th>R7154 - UV/Solar Blind</th>
<th>R106 - UV/Visible Broadband</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral response</td>
<td>160 - 320 nm</td>
<td>160 - 650 nm</td>
</tr>
<tr>
<td>Wavelength of maximum response</td>
<td>254 nm</td>
<td>340 nm</td>
</tr>
<tr>
<td>Photocathode Material</td>
<td>Cs-Te</td>
<td>Sb-Cs</td>
</tr>
<tr>
<td>Minimum effective area</td>
<td>8 x 24 mm</td>
<td>8 x 24 mm</td>
</tr>
<tr>
<td>Window material</td>
<td>Quartz</td>
<td>Fused silica</td>
</tr>
<tr>
<td>Dynode Secondary emitting surface</td>
<td>Sb-Cs</td>
<td>not given</td>
</tr>
<tr>
<td>Number of stages</td>
<td>9</td>
<td>9</td>
</tr>
</tbody>
</table>

Figure 2.15: Quantum efficiencies of PMTs used in the $S_2$ cross section measurements

2.4 Data Collection Trips

In September 2013, we made a preliminary trip to NIST to meet with Dr. Gillian Nave and discuss the $S_2$ measurements. We tested the 1000 W Xenon (Xe) emission lamp, a continuum light source in the UV. We also explored several different spectral ranges, using a variety of PMTs and optical filters.
We assessed the signal-to-noise ratio (S/N) of each combination of detector and optical filter. Specifically, we found that the broadband Hamamatsu R106 PMT with a UG5 filter has S/N = 25 at the peak transmission for one five-minute scan at a resolution of 0.1 cm$^{-1}$. Thus, we predicted that high resolution scans with S/N = 100 would require 80 minutes. We chose to work at a resolution of 0.1 cm$^{-1}$ because the thermal Doppler width of a spectral line at 200°C is approximately 0.1 cm$^{-1}$. We cannot resolve the line structure beyond the Doppler width. Additionally, the combination of the R106 PMT and UG5 filter allowed us to observe wavelengths longer than 315 nm, necessary for observing the (0-0) vibrational band in S$_2$ and determining the presence of contaminating allotropes such as S$_3$.

We planned to make the S$_2$ measurements in October. However, the federal government shut-down delayed the trip until December. Prior to the December trip, a full system test was run at Wellesley in November.

2.4.1 December 2013

We returned to NIST for two days in early December 2013 with the absorption cell, furnace, and temperature controller to make our first set of measurements. Based on the full system tests at Wellesley in November 2013, spring 2013, and summer 2012, we expected to observe S$_2$ in the cell at an absorption cell temperature of 700°C and a side-arm temperature of 170°C. But the absorption signal using the NIST FTS was an order of magnitude deeper than absorption detection on the 1-m grating spectrometer, SPEX 1702, at Wellesley College. The NIST FTS has 10 times greater resolution than the Wellesley grating spectrometer. We began to observe S$_2$ signatures at approximately a side-arm temperature of 100°C. The absorption signal was too deep and the absorption peaks saturated.
Over the course of this trip, we finalized our choices of PMT and optical filter. We chose the UV/Solar blind Hamamatsu R7154 PMT with UG5 (spectral range: approximately 300 to 235 nm, or 32,500 to 42,500 cm\(^{-1}\)) to measure the broadened vibrational bands and search for evidence of an \(S_2\) continuum. We also selected the UV-visible broadband Hamamatsu R106 PMT with UG5 filter (spectral range: approximately 445 to 235 nm, or 22,500 to 42,500 cm\(^{-1}\)) for measuring the sharp rotational bands in \(S_2\). In addition, this combination’s spectral range overlaps with regions of large cross section in \(S_3\), allowing us to search for contaminating allotropes (Billmers & Smith 1991). Table 2.3 lists several important characteristics of each PMT. Figure 2.15 shows the quantum efficiency of each PMT\(^{10}\). Low quantum efficiency reflects the PMT’s inability to detect that light effectively. Thus, the quantum efficiency curve describes the spectral range detected by the PMT. Figure 2.16 is the transmittance of the UG5 filter as a function of wavelength (nm)\(^{11}\). The overlap in quantum efficiency of each PMT with the filter’s transmittance curve describes the spectral range of each combination. Figure 2.17 displays the spectral ranges of each combination.

The small spikes are emission peaks in the Xe continuum.


Figure 2.17: Spectral ranges of the chosen PMT and optical filter combinations

(a) UV/Solar blind PMT + UG5

(b) UV-visible PMT + UG5
We also learned that the high temperature of the absorption cell conduction block (700°C) warmed the bottom of the cell as well, causing the temperature of the side arm to gradually increase. At 170°C, the side arm was sufficiently warm that this effect was negligible. Unfortunately, the thermal drift was noticeable at the lower side-arm temperatures (100-140°C) required to achieve 50% absorption in the spectra. The temperature stability of the side arm is paramount for establishing a stable column density. For this reason, we planned to make measurements in January at an absorption cell temperature of 550°C, rather than 700°C.

Although Meyer predicted that only 80% of the saturated vapor in the cell would be S₂ at 800 K (approximately 530 °C) and 100 torr, we were working with much smaller vapor pressures and never observed the presence of other allotropes. Preliminary searches for S₃ and S₄ at Wellesley in summer 2012 indicated clean spectra of S₂ with absorption cell temperatures as low as 600°C. Billmers & Smith reported that the S₃ cross section peaks around 400 nm, and therefore would be clearly visible in our spectral range. An additional benefit of using a lower temperature is lower thermal populations of the ground electronic state (figure 3.9), simplifying the spectrum. Table 2.4 supplies the vibrational population distribution (Boltz = Boltzmann Factor) of the ground electronic state at 550°C and 700°C. Fewer populated vibrational levels in the electronic ground state results in fewer possible vibrational bands, simplifying the spectrum. The energies were calculated using Dr. Gibson’s CSE program (see section 3.2.2). Additionally, at lower temperature, fewer rotational levels are populated (see figure 3.9).

<table>
<thead>
<tr>
<th>ν&quot;</th>
<th>Energy (cm⁻¹)</th>
<th>Boltz (550°C)</th>
<th>Boltz (700°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>362.2</td>
<td>0.716</td>
<td>0.644</td>
</tr>
<tr>
<td>1</td>
<td>1082.3</td>
<td>0.203</td>
<td>0.239</td>
</tr>
<tr>
<td>2</td>
<td>1796.5</td>
<td>0.0578</td>
<td>0.0818</td>
</tr>
<tr>
<td>3</td>
<td>2504.8</td>
<td>0.0167</td>
<td>0.0295</td>
</tr>
<tr>
<td>4</td>
<td>3207.1</td>
<td>4.87×10⁻³</td>
<td>0.0107</td>
</tr>
<tr>
<td>5</td>
<td>3904.2</td>
<td>1.43×10⁻³</td>
<td>3.94×10⁻³</td>
</tr>
</tbody>
</table>

Table 2.4: Vibrational population distribution of S₂ ground electronic state
2.4.2 January 2014

In January 2014, we completed the S$_2$ cross section measurements at NIST over the course of two days. We collected high resolution spectra at seven distinct column densities, determined by their different side-arm temperatures, at an absorption cell temperature of 550°C. The NIST spectrometer has two outputs. We connected a different PMT-filter combination to each output to collect two spectral ranges simultaneously. The UV/Solar blind R7154 PMT with 1mm UG5 filter monitored channel A while the UV-visible R106 PMT with 1mm UG5 filter monitored channel B. Table 2.5 summarizes the measurements made.

<table>
<thead>
<tr>
<th>Description</th>
<th>Resolution (cm$^{-1}$)</th>
<th># Coadds</th>
<th>AC Temp (°C)</th>
<th>SA Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>blank</td>
<td>1</td>
<td>64</td>
<td>485-530</td>
<td>30.7</td>
</tr>
<tr>
<td>blank</td>
<td>1</td>
<td>64</td>
<td>522-551</td>
<td>37.4</td>
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<td>64</td>
<td>550</td>
<td>40-43C</td>
</tr>
<tr>
<td>120°C</td>
<td>0.1</td>
<td>115</td>
<td>550</td>
<td>119.75</td>
</tr>
<tr>
<td>130°C</td>
<td>0.1</td>
<td>134</td>
<td>550</td>
<td>129.38</td>
</tr>
<tr>
<td>140°C</td>
<td>0.1</td>
<td>101</td>
<td>550</td>
<td>139.2</td>
</tr>
<tr>
<td>155°C</td>
<td>0.1</td>
<td>75</td>
<td>550</td>
<td>154.7</td>
</tr>
<tr>
<td>175°C</td>
<td>0.1</td>
<td>48</td>
<td>550</td>
<td>174.49</td>
</tr>
<tr>
<td>195°C</td>
<td>0.1</td>
<td>40</td>
<td>550</td>
<td>194.58</td>
</tr>
<tr>
<td>Day 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>blank</td>
<td>1</td>
<td>64</td>
<td>500-520</td>
<td>21.5</td>
</tr>
<tr>
<td>hot blank</td>
<td>1</td>
<td>64</td>
<td>550</td>
<td>30.7</td>
</tr>
<tr>
<td>175°C</td>
<td>0.1</td>
<td>75</td>
<td>550</td>
<td>174.49</td>
</tr>
<tr>
<td>195°C</td>
<td>0.1</td>
<td>55</td>
<td>550</td>
<td>194.58</td>
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<tr>
<td>215°C</td>
<td>0.1</td>
<td>75</td>
<td>550</td>
<td>214.74</td>
</tr>
</tbody>
</table>

*Table 2.5: January 2014 S$_2$ measurements*
A note about measuring the background intensity, or ‘blank,’ for the $S_2$ measurements: Unfortunately, it is not possible to remove the $S_2$ absorption cell from the optical path nor purge the gas inside between scans. Therefore, a blank cannot be collected before and after each scan, to monitor drift in the continuum or variations in intensity. The cell is enclosed in the furnace system, which was too hot to be moved in and out of the optical path. The warm up time for the furnace is approximately 90 minutes and it is not possible to quench the sulfur well between measurements. Consequently, all blanks must be taken at the start and end of each day, and while heating up the absorption cell before sufficient vapor forms.
Chapter 3

Theory

This chapter describes the general characteristics and theory of molecular absorption, discusses the electronic structure of diatomic sulfur, $S_2$, and outlines the theory behind the column density estimate presented in chapter 4.

Molecules demonstrate four kinds of motion - electronic, vibrational, rotational, and translational. The Hamiltonian, or quantum mechanical operator corresponding to the total energy $E$ of the system, accounts for all the energies associated with these motions. The full molecular Hamiltonian is:

$$\hat{H} = T^N(R) + H^{\text{rot}}(R, \theta, \phi) + T^e(r) + V(r, R) + H^{SO} + H^{SS} + H^{SR},$$

(3.1)

where the first four terms comprise the non-relativistic molecular Hamiltonian. $R$ represents the internuclear separation. $\theta$ and $\phi$ give the angular position of the internuclear axis relative to the fixed lab axis. $r$ represents the positions of the electrons. $T^N$ and $H^{\text{rot}}$ together describe the kinetic energy associated with nuclear vibrations and rotations. $T^e$ accounts for the kinetic energy of the electrons. $V$ summarizes the electrostatic potential energy of the interactions among the electrons and nuclei. The last three terms arise from interactions.

\footnote{All kinetic and potential energy in the system}
(spin-orbit, spin-spin, and spin-rotation, respectively) between the intrinsic magnetic dipole moment of the electrons and their dipole moments associated with their orbital motion. The full molecular Schrödinger equation cannot be solved analytically.

The Born-Oppenheimer Approximation, discussed next, allows the molecule’s wave function to be decomposed into electronic and nuclear components. The nuclear motion is further broken down into vibrational and rotational motion. The approximation allows us to first calculate the electronic wave function, then the vibrational wave function, which describes the oscillations of the nuclei. The molecule’s rotational motion (term $H_{\text{rot}}$ in equation 3.1) is treated as a perturbation in the Born-Oppenheimer basis, as are the relativistic terms. These perturbations will be considered later. The molecule’s translational energy is spectroscopically boring and often ignored, since the molecule’s translational motion is unaffected by its molecular structure.  

### 3.1 The Born-Oppenheimer Approximation

The non-relativistic molecular Hamiltonian is:

$$
\hat{H} = -\frac{\hbar^2}{2} \sum_\alpha \frac{1}{M_\alpha} \nabla^2_{R_\alpha} - \frac{\hbar^2}{2m_e} \sum_i \nabla^2_{r_i} + \frac{Z_\alpha Z_\beta e^2}{4\pi \epsilon_0 R} + \sum_i \sum_{j>i} \frac{e^2}{4\pi \epsilon_0 r_{ij}} - \sum_\alpha \sum_i \frac{Z_\alpha e^2}{4\pi \epsilon_0 r_{\alpha i}},
$$

where the Greek letters, $\alpha$ and $\beta$, represent each nucleus while the Roman letters, $i$ and $j$, represent the electrons. $R$ represents the internuclear separation. $r_i$ represents the vector position of each electron with respect to the origin of the chosen coordinate system. $R_\alpha$

---

2The particle’s velocity, determined by its temperature, as it translates through space affects its spectrum through a process called **thermal Doppler broadening**. The absorbing particles’ thermal motion causes variations in the energy of the absorbed photons. The energy of a photon is proportional to its frequency. Thus, the variations in absorbed energy correspond to variations in frequency, governed by the Doppler Effect. Transition frequencies of particles approaching the light source shift to higher frequencies, while frequencies of those moving away shift to lower frequency. Overall, particles moving both directions lead to a wider bandwidth of photon frequencies producing the same transition. Spectroscopically, this results in the broadening of each transition line in the spectrum.
represents the vector position of each nucleus with respect to the origin. Numbering from the left, the terms are:

1. Kinetic energy of the nuclei
2. Kinetic energy of the electrons
3. Potential energy of the repulsion between the nuclei
4. Potential energy of the repulsion between the electrons
5. Potential energy of the attraction between the electrons and nuclei

The last three terms are electrostatic potential energies resulting from the Coulomb interactions among the electrons and nuclei. They replace $V(r, R)$ in equation 3.1.

Unfortunately, the non-relativistic molecular Schrödinger equation cannot be solved analytically. The **Born-Oppenheimer Approximation** simplifies the molecular Hamiltonian to the “electronic” Hamiltonian by assuming a constant internuclear separation ($R = \text{constant}$). We can assume a constant internuclear separation because the nuclei are much more massive than the electrons and therefore much slower, relative to the electrons. Since they are so much slower, it is sensible to ‘fix’ the nuclei’s positions relative to the electrons, thus fixing the internuclear distance.

Fixing the internuclear distance simplifies the molecular Hamiltonian (equation 3.2) by eliminating terms (1) and (3). Term (1) depends on derivatives of the nuclei’s positions. The positions are fixed, so their derivatives are zero. Term (3) becomes a constant set by the internuclear separation, $R$. Constants do not affect wave functions, so we can safely neglect this term for now. Constants do shift eigenvalues, however, so we will have to restore this term later to calculate the total energy of the system.
Having made the Born-Oppenheimer Approximation, the molecular Hamiltonian simplifies to the electronic Hamiltonian, containing terms (2), (4), and (5):

\[ \hat{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_i \nabla^2 r_i + \sum_i \sum_{j>i} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{\alpha} \sum_i \frac{Z_\alpha e^2}{4\pi\epsilon_0 r_{\alpha i}}. \] (3.3)

We can solve the Schrödinger Equation for the electronic Hamiltonian, \( \hat{H}_{el}\psi_{el} = E_{el}\psi_{el} \). The solutions are the electronic wave functions, \( \psi_{el}(r; R) \). Each is a function of all the electronic coordinates, \( r \), and one internuclear separation distance, \( R \). For each \( R \), there is a new \( \psi_{el} \). \( E_{el} \) is the electronic energy eigenvalue associated with a given \( \psi_{el} \) and, thus, with a given \( R \). The electronic wave functions collectively form a basis. A superposition of these basis functions can be used to express the system’s true wave function.

### 3.1.1 Potential Energy Curves

We must restore the constant nuclear repulsion term (term (3) in equation 3.2) for the total electronic energy associated with each state (each \( \psi_{el} \)). Thus,

\[ U(R) = E_{el}(R) + \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 R}. \] (3.4)

The function, \( U(R) \), represents a potential energy curve. Such a curve exists for each electronic state, \( \psi_{el} \). Notice the parametric dependence on the internuclear separation, \( R \). The Born-Oppenheimer Approximation assumes that the electrons immediately readjust to changes in \( R \). (Recall that the electrons move much more quickly than the more massive nuclei.) The energy of the electrons immediately changes to \( E_{el}(R') \) from \( E_{el}(R) \) in the event that the internuclear separation changes to \( R' \) from \( R \). Figure 3.2 displays potential energy curves in \( S_2 \). They will be discussed later.

While potential energy curves are not physical things, they are useful devices. We
can treat them as the potential in which the nuclei of the molecule move. The nuclei can be thought of as moving and vibrating in these potential energy wells, like harmonic oscillators. We arrive at the vibrational structure of each electronic state by evaluating this nuclear motion. We recover the rotational structure of the molecule by restoring the perturbative terms of the full molecular Hamiltonian (equation 3.1). A brief overview of this process is given in section 3.4.3.

In this way, the molecular energy structure can be broken down into a series of nested energy levels. The electronic Hamiltonian yields the potential energy curves of each electronic state. Within each electronic state, the quantized motion of the nuclei along on the internuclear axis leads to a set of vibrational states. The vibrational levels can be further split into rotational levels, by considering the change in the nuclei’s angular position.

3.1.2 The Nuclear Hamiltonian

Combining the potential energy curve, $U(R)$, with the nuclear kinetic energy term ((1) in equation 3.2) forms the nuclear Hamiltonian, for which the Schrödinger Equation can be solved. The nuclear Hamiltonian is:

$$\hat{H}^N = -\frac{\hbar^2}{2} \sum_\alpha \frac{1}{M_\alpha} \nabla^2_{R_\alpha} + U(R) = -\frac{\hbar^2}{2} \sum_\alpha \frac{1}{M_\alpha} \nabla^2_{R_\alpha} + \left( E_{el}(R) + \frac{Z_\alpha Z_\beta e^2}{4\pi\epsilon_0 R} \right). \quad (3.5)$$

This form of the nuclear Hamiltonian treats both the translational and rotational motion of the nuclei. In the Born-Oppenheimer Approximation, angular motion is considered a perturbation on the system. Therefore, the angular positions of the nuclei are held constant. As a result, the Laplacian in term (1) of equation 3.5 reduces to the partial second derivative of the nuclear wave function with respect to each nucleus’ position with respect to the origin of the chosen coordinate system, $R_\alpha$. Thus, the Schrödinger Equation for the nuclear motion
is:

\[
\left\{ -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{M_{\alpha}} \frac{\partial^2}{\partial R_{\alpha}^2} + U(R) \right\} \psi_N = \varepsilon \psi_N.
\] (3.6)

The energy, \( \varepsilon \), is the total electronic and vibrational energy of the molecule, as calculated by the Born-Oppenheimer Approximation. The total wave function is \( \Psi(r,R) = \psi_{el}(r;R)\psi_N(R) \). Appendix A provides a more formal justification for this approach.

### 3.1.3 Alternative Forms of the Born-Oppenheimer Approximation: Adiabatic and Diabatic Wave Functions

The wave functions discussed above are the adiabatic wave functions. They are associated with states whose dominant electron configurations change with the internuclear separation, \( R \). Their associated potential energy curves, \( U(r;R) \) (equation 3.4), are called the adiabatic potential energy curves. Another form of the Born-Oppenheimer ignores the electron-electron electrostatic repulsion term (term (4) in equation 3.2) but includes the nuclear kinetic energy term, \( T^N \). This form produces the diabatic basis of wave functions and potential energy curves, associated with a single electron configuration. Both the adiabatic and diabatic bases are valid representations of the electronic states of a diatomic molecule. The true wave functions can be expressed as superpositions of either set of basis functions. One chooses to work in the basis in which the Hamiltonian has the fewest off-diagonal matrix elements, in order to simplify calculations.

From now on, the electronic wave functions, previously \( \psi_{el} \), will be referred to as \( \phi^{a/d} \) where \( a \) indicates the adiabatic basis and \( d \) indicates the diabatic basis. The rotationless nuclear wave functions, \( \psi_N \), will be referred to as the vibrational wave functions of the molecule, \( \chi_{i,v} \). For further information, please consult Lefebvre-Brion 2004.
3.2 Calculating Potential Energy Curves and Wave Functions

In order to make predictions about the behavior of the molecule, it is necessary to calculate the potential energy curves and the molecular wave functions described in section 3.1. This section briefly describes the computational methods employed in this work to produce the potential energy curves and wave functions.

3.2.1 The Rydberg-Klein-Rees Method for Potential Energy Curves

The Rydberg-Klein-Rees (RKR) method, discussed extensively by Yomay Shyur ‘11 in her thesis, is one approach for determining the potential energy curves of diatomic molecules. This approach calculates the classical turning points of a potential energy curve using measured vibrational energy levels and rotational constants. Then, by treating the vibrational quantum number as a continuous variable, the RKR method smoothly joins the turning points to form a potential curve. This thesis employs an RKR program developed by Dr. Steve Gibson of the Australian National University. The program produces the potential energy, $E$, in electron-volts as a function of internuclear separation, $R$, in angstroms. It also offers two different approaches for calculating the outer limb of the potential energy curve, the region beyond the scope of the supplied vibrational levels. It models the outer limb using either a Morse potential or a “LeRoy extension.” The Morse potential is given by:

$$V_m(R) = D_e \left(1 - e^{-a(R-R_e)}\right)^2,$$  \hspace{1cm} (3.7)
Figure 3.1: Potential energy curve of the $S_2$ ground electronic state, as generated by Dr. Gibson’s RKR program. The green dots represent the calculated turning points based on supplied spectroscopic information. The blue curve represents the resulting potential curve.
where $D_e$ is the dissociation energy, $a$ is a coefficient, and $R_e$ is the equilibrium length of the bond between the nuclei. The LeRoy extension is:

$$V_i(R) = D_e + \sum_k C_k \frac{1}{R^k}$$  \hspace{1cm} (3.8)

where $C_k$ are coefficients. This work uses potential energy curves with the Morse potential.

### 3.2.2 The Coupled Schrödinger Equation Method

Having calculated the potential energy curves, we can calculate the wave functions in the diabatic Born-Oppenheimer basis,

$$\Psi_n(r, R) = \sum_{i=1}^N \sum_{v=0}^\infty c_{n,i,v}^d(\phi_d^i(r, R)\chi_{i,v}(R).$$  \hspace{1cm} (3.9)

$n$ indexes the full wave function. $i$ indexes $N$ electronic states. $v$ is the vibrational quantum number, corresponding to the index of the vibrational level of the molecule. There are three ways to tackle the Schrödinger Equation:

1. Diagonalize the matrix version of the full Hamiltonian in the basis of equation 3.9
2. Use perturbation theory
3. Use the Coupled Schrödinger Equation (CSE) method

In theory, we could represent the full Hamiltonian in the diabatic Born-Oppenheimer basis and diagonalize it to reveal the true vibronic molecular energies. Unfortunately, that Hamiltonian has an infinite number of terms and so cannot be diagonalized. Ordinarily, we would truncate the Hamiltonian by neglecting higher vibrational levels. This treatment is unrealistic when the electronic state interactions involve many vibrational levels, including

---

3"Vibronic" refers to the total electronic and vibrational energy.
those levels in the continuum (beyond the dissociation limit of the molecule). When these interactions, represented by off-diagonal matrix elements in the Hamiltonian, are large, a truncated Hamiltonian poorly describes the system. Without truncation, the Hamiltonian matrix is too large for direct diagonalization.

Perturbation theory is similarly frustrated when higher vibrational levels are important for determining the true vibronic energy levels. Perturbation theory only holds for weak interactions. According to perturbation theory, a Hamiltonian, $\hat{H}$, can be described as the sum of an ‘unperturbed’ Hamiltonian, $H_0$, and a perturbation term, $W$, formed from the off-diagonal elements of $\hat{H}$ - hence $\hat{H} = H_0 + W$. However, if the perturbation, $W$, is large (meaning it represents strong interactions), then this method fails. Perturbation theory is a common approach, derived in many textbooks on quantum mechanics including Griffiths 2005. The less-well known CSE method, however, can calculate the exact energy levels of coupled electronic states, even if the states are strongly interacting (as in the case of $S_2$’s electronic states).

In the CSE method, we expand the true wave functions of the interacting states’ full Hamiltonian (neglecting rotations and intrinsic spin) in the diabatic Born-Oppenheimer basis (equation 3.9). We combine the coefficients, $c_{i,v}$, and vibrational wave functions, $\chi_{i,v}$, from equation 3.9 into numeric functions, $f_{n,i}(R)$:

$$\Psi_n(r, R) = \sum_{i=1}^{N} \phi_i^d(r, R)f_{n,i}(R).$$  

(3.10)

The set of numeric functions weight the diabatic electronic wave functions, $\phi_i^d$, allowing us to find exact solutions for the energy levels of the coupled electronic states. Unfortunately, it is impossible to determine which superposition of vibrational states was used to calculate the vibronic energy. Lucy Archer ’12 mathematically describes the CSE approach and compares perturbation theory and the CSE method in chapter 3 of her thesis.
3.3 Electronic Structure of Diatomic Sulfur

This section takes a detailed look at the characteristics of the potential energy curves of the electronic states of $S_2$.

Each electronic state can be represented by a potential energy curve, as shown in section 3.1 equation 3.4. Spectroscopists denote electronic states in several ways. First, electronic states are often classified according to their angular momenta, $^{2S+1}A\Omega$, where $S$ is the intrinsic spin of the electrons, $A$ represents the projection of the total orbital angular momentum on the internuclear axis, and $\Omega$ is the projection of total angular momentum on the internuclear axis. For example, the ground state of $S_2$ has integer spin ($S=1$), and no orbital angular momentum ($A=0 \rightarrow \Sigma$). $\Omega$ equals integer steps from $A + \Sigma = 0 + 1 = 1$ to $A - \Sigma = 0 - 1 = -1 \rightarrow \Omega = -1, 0, 1$. Therefore, the spectroscopic label for the ground state is $^3\Sigma_{-1,0,1}$. Second, the electronic levels’ relative energies are designated by an alphabetical labeling scheme. The ground electronic state is conventionally labelled X. The second lowest energy state is A, then B, and so on. Frequently, an intervening energy level is discovered between two previously-known levels. Rather than adjust the entire naming scheme, such levels are designated by a primed letter. For example, the $S_2 B''$ state was found later between the B and C states.

Many vibrational levels, representative of the quantized vibrations of the nuclei within the electronic potential, exist in each electronic level. They are labelled by the vibrational quantum number, $v$. In addition to the vibrational levels, there are rotational levels, describing the quantized rotations of the nuclei, marked by the angular momentum quantum number, $J$. The energy difference, or ‘spacing,’ between two electronic levels is typically much greater than that between two vibrational levels. The spacing between subsequent

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4 $A$ is replaced by a capitalized Greek letter corresponding to the value of the total orbital angular momentum. $\Sigma = 0, \Pi = 1, \Delta = 2$ then continuing alphabetically

5 $\Omega$ = projection of the total orbital angular momentum on the internuclear axis + the projection of the intrinsic spin on the internuclear axis. $\Omega = \Lambda - \Sigma$ to $\Lambda + \Sigma$ in integer steps.
vibrational levels is much greater than that between two rotational levels.

When discussing a particular state of the molecule, its electronic level, vibrational level, and rotational level must be specified. For example, the lowest rovibrational level of the molecule in the ground electronic state is expressed as X(v=0,J=0). However, various aspects of this notation are often omitted if they can be derived from context. When describing a transition, all lower state quantum numbers are double-primed (e.g. v''), while those of the upper state are marked with a single prime (e.g. J').

The shape of an electronic state’s potential energy curve, as given by equation 3.4, describes the likely fate of the molecule’s nuclei. If the potential energy curve contains a well, then the nuclei behave approximately like quantum harmonic oscillators. This type of curve is considered a stable, bound state of the molecule. However, if the potential energy curve does not contain a well, then the relative motion of the nuclei is unconstrained, allowing the nuclei of the molecule to fly apart. This type of curve indicates an unstable, unbound state of the molecule, often called a **dissociating** state. Figure 3.2 displays calculated diabatic potential curves for S₂. Both the X and B states are bound, while the B'' state dissociates.
Recall that the diabatic states result from the Born-Oppenheimer Approximation. The true energy states of the molecule are linear combinations of these diabatic curves shown in figure 3.2.

Absorption transitions from the ground electronic state, $X^{3}\Sigma_g^{-}$, to the excited electronic state, $B^{3}\Sigma_u^{-}$, dominate UV absorption by $S_2$ from 250-310 nm. The $-$ and $u$ labels indicate symmetries of the electronic states:

- Switching the nuclei multiplies the electronic wave function by $\pm 1$. An unaffected electronic wave function ($\times 1$) has *gerade* (German for ‘even’) symmetry, marked by a subscript $g$. An electronic wave function multiplied by -1 has *ungerade* (‘odd’) symmetry, denoted by a subscript $u$. Both $S_2$ electronic states considered here are ungerade.

- The electronic states are marked with a superscript $\pm$, denoting the symmetry of the electronic wave functions if they are reflected over a plane through the internuclear axis of the molecule. $+$ indicates that the wave function is unchanged; $-$ indicates that its sign changed.

The presence of the dissociating $B''$ state complicates the B-X system by perturbing the B state, leading to a phenomenon called *predissociation*, discussed in section 3.3.2. It is relevant that both the X and B states are *triplet* states, meaning that they have intrinsic spin, $S$, equal to 1. For every singlet-singlet ($S=0$) transition line, a triplet-triplet has three. Figure 3.3 compares the modeled vibrational bands of a singlet-singlet ($^{1}\Sigma^{-}-^{1}\Sigma$) and a triplet-triplet ($^{3}\Sigma^{-}-^{3}\Sigma$) transition spectrum at room temperature (295 K). The models were generated using PGopher.

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6PGOPHER, a Program for Simulating Rotational Structure, C. M. Western, University of Bristol, [http://pgopher.chm.bris.ac.uk](http://pgopher.chm.bris.ac.uk)
(a) Singlet ($S=0$) - Singlet transitions at room temperature, modeled in PGopher

(b) Triplet ($S=1$) - Triplet transitions at room temperature, modeled in PGopher

*Figure 3.3:* Comparing $^1\Sigma^-^1\Sigma$ and $^3\Sigma^-^3\Sigma$ transitions. Note the plethora of additional lines in the triplet-triplet transition.
### 3.3.1 Calculating Rovibrational Energy Levels

\[ E_{\text{vib}} = G(v) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 \quad (3.11) \]

\[ E_{\text{rot}} = F(J) = B (J (J + 1)) - D (J (J + 1))^2 \quad (3.12) \]

Section 3.2.1 described a method for calculating the potential energy of an electronic state. Absorption and emission spectroscopy, however, illuminate the vibrational and rotational energy level structure of a molecule. Equations 3.11 and 3.12 describe approximations for calculating the energies of these levels. Equation 3.11 for the vibrational energy, \( G(v) \), is the energy of a quantum harmonic oscillator, plus an anharmonic correction term. The first term of equation 3.12 for the rotational energy, \( F(J) \), is the energy of a rigid rotor, where \( B = \frac{\hbar^2}{2I} \) and \( I \) is the rotational inertia of the molecule\(^7\) which is again followed by a higher order correction term, this time representing the centrifugal distortion of the rotating molecule (Demtröder 2005). In both equations, higher order correction terms beyond the first have been ignored.

Each electronic state contains both vibrational and rotational levels. Thus the total energy of a rovibrational level relative to the minimum of the electronic potential energy curve is:

\[ E_{v,J} = G(v) + F(J) = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + B (J (J + 1)) - D (J (J + 1))^2. \quad (3.13) \]

Note that in order to accurately represent the true energy of level \((v,J)\), additional correction terms must be included. Finally, the total energy of a state of the molecule is the sum of the electronic and nuclear energies - thus the sum of the electronic, vibrational, and rotational energies. The energy of a transition in the molecule is the difference between the upper and lower energy states (Demtröder 2005).

\(^7I = \mu R^2\): \( \mu \) is the reduced mass of the nuclei and \( R \) is the internuclear distance
3.3.2 Predissociation

Figure 3.4: Onset of predissociation in S\textsubscript{2}. The red line records the background intensity. (absorption cell temperature = 550°C, side-arm conduction block temperature = 140°C, solar blind photomultiplier tube)

Predissociation occurs when a bound state, like the B state of S\textsubscript{2}, shares a non-zero off-diagonal matrix element with another electronic state of lower dissociation energy. Conventionally, states sharing non-zero off-diagonal matrix elements are said to ‘interact.’ The resulting states blend characteristics of the bound wave functions of the bound potential and the dissociating wave functions of the unstable or lower-dissociation energy state. In other words, the true wave functions are superpositions of bound and dissociating wave functions. Therefore, the states of the nominally bound potential energy curves, which would other-
wise exhibit approximately harmonic vibrations of the nuclei, have a nonzero probability of dissociating (Shyur 2011).

We can experimentally detect predissociated states using absorption spectroscopy. The radiative lifetime\(^8\) of a predissociated state is much shorter than that of its unperturbed equivalent. Due to the Heisenberg Uncertainty relation between time and energy intervals, the photon bandwidth capable of triggering a transition widens, resulting in the broadening of a spectral line.

Figure 3.4 shows a portion of one of the \(S_2\) spectra collected in January 2014. It clearly depicts the onset of predissociation of the vibrational levels of the B state above \(v' = 10\), as reported in Wheeler et al. Notice that the discrete rotational structure of the (9-0) band is clearly visible, while the (10-0) band shows some broadening (possibly a result of the overlapping, predissociating (11-1) band) and the (11-0) band is completely diffuse. Eventually, the dissociating character dominates, indicated in the spectrum by continuum absorption (figure 3.5). Further work includes modeling the predissociation mechanism in \(S_2\) in detail. Additionally, there are three more upper states interacting with the B and \(B''\) states. A thorough model of \(S_2\) must account for the interactions among all five states.

\(^8\)Section 3.4.2 discusses radiative lifetimes in detail
Figure 3.5: The $S_2$ spectrum has an absorption continuum beginning at about 40,000 cm$^{-1}$. The red line records the blank intensity. (absorption cell temperature = 550°C, side-arm conduction block temperature = 155°C, solar blind photomultiplier tube)

### 3.3.3 Transitions

This section discusses the allowed electric dipole transitions in $S_2$.

The total angular momentum of a molecule is the sum of the molecule's total orbital, intrinsic (spin), and rotational momenta: $J = L + S + R$. A second useful quantum number, $N$, is defined as the difference between the total angular momentum and the spin, equivalent to the sum of the orbital and rotational momentum: $N = J - S = L + R$.

Only transitions resulting in a change in total angular momentum quantum number,
\( \Delta J \), of \( \pm 1 \) or 0 are possible by the electric dipole mechanism. This selection rule can be derived from the electric dipole operator. There are no selection rules for \( \Delta N \). The numeric values of \( \Delta J \) and \( \Delta N \) are represented by letters. P indicates a change of -1. R marks a change of +1. Q represents no change in quantum number. Each \( \Delta J \) group constitutes a branch of transitions. For example, all transitions with \( \Delta J=+1 \) are in the R-branch. The strongest branches, called the main branches, have \( \Delta N=\Delta J \). The other branches are called satellite branches.

We identify transitions by their change in \( \Delta N \), change in total angular momentum quantum number, \( \Delta J \), and their lower level total angular momentum quantum number, \( J'' \). A transition is represented in spectroscopic notation by \( ^{\Delta N\Delta J}F_{F'}F''(J'') \) where each subscript \( F \) is replaced by that level’s ‘F’ designation, and \( J'' \) is replaced by the value of the total angular momentum quantum number of the lower state. The ‘F’ designation for each level indicates the relationship between the total angular momentum quantum number, \( J \), and the pattern forming quantum number, \( N \):

- \( F_1 \): \( J=N+1 \)
- \( F_2 \): \( J=N \)
- \( F_3 \): \( J=N-1 \)

<table>
<thead>
<tr>
<th>Main Branch</th>
<th>( \Delta N )</th>
<th>( \Delta J )</th>
<th>( F' )</th>
<th>( F'' )</th>
<th>Lowest ( J'' )</th>
<th>Satellite Branch</th>
<th>( \Delta N )</th>
<th>( \Delta J )</th>
<th>( F' )</th>
<th>( F'' )</th>
<th>Lowest ( J'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^R R_{3,3}(0) )</td>
<td>+1</td>
<td>+1</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>( ^P R_{1,3}(0) )</td>
<td>-1</td>
<td>+1</td>
<td>1</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>( ^R R_{2,2}(1) )</td>
<td>+1</td>
<td>+1</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>( ^P Q_{1,2}(1) )</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( ^R R_{1,1}(2) )</td>
<td>+1</td>
<td>+1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>( ^R Q_{3,2}(1) )</td>
<td>+1</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>( ^P P_{1,1}(2) )</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
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<td>( ^R P_{3,1}(2) )</td>
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<td></td>
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<td></td>
<td></td>
<td>( ^N P_{1,3}(2) )</td>
<td>-3</td>
<td>-1</td>
<td>1</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
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<td></td>
<td>( ^P Q_{2,3}(2) )</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

| Table 3.1: Branches of allowed electric dipole transitions in the B-X system in \( S_2 \) |

For example, a transition with \( \Delta N=-1, \Delta J=+1 \) originating at \( J''=0 \), is represented in spectroscopic notation as \( ^P R_{13}(0) \). It is a member of the “p-form R branch.” Figure 3.6 depicts
the 14 distinct branches of allowed electric dipole transitions in the B-X system in \( S_2 \) (listed in table 3.1). It also marks some useful symmetries and parities of the different rotational levels in the B-X system:

- **Rotationless parity** - It is convenient to know the parity of the rotationless orbital wave function. A rotation level with quantum number \( J \) is designated with a \( e \) if it has a parity of \((-1)^J\). It is marked with an \( f \) if it has a parity of \((-1)^{J+1}\) (Brown & Carrington 2003).

- **Symmetric/antisymmetric orbital wave function** - Switching the labels of the nuclei either multiplies the whole wave function by -1 (antisymmetric, \( a \)) or it remains the same (symmetric, \( s \)). The \( S_2 \) nuclei are identical bosons, so the total wave function must be symmetric. However, they are also spinless so they do not have a spin wave function. Therefore, all the orbital wave functions must be symmetric to ensure that the full wave function is symmetric.

- **Overall parity** - The parity operator, \( P \ket{x, y, z} \rightarrow P \ket{-x, -y, -z} \), multiplies every coordinate by -1. If a wave function operated on by the parity operator does not change, then it has even parity (+). If operation with the parity operator changes the sign of the wave function, then the wave function has odd parity (−).
Figure 3.6: Chart of the branches of the allowed electric dipole transitions in the B-X system in $S_2$
3.4 Calculating Column Density

There are many ingredients necessary to derive the cross section of a molecule. This thesis seeks to solve for the cross sections of S\textsubscript{2} in the UV using the column density calibration scheme proposed by Professor Stark and Yomay Shyur ‘11 in her thesis. The rest of this chapter concentrates on deriving the necessary relationships to extract a column density from a measured spectrum. Using these calculations, chapter 4 presents an estimate of the column density for one of the spectra collected in January 2014 at NIST.

3.4.1 Measuring Absorption: the Beer-Lambert Law

In order to measure light absorption by a gas, spectroscopists direct a light source of known intensity through a sample of the gas and measure the intensity of the transmitted beam as a function of wavelength. By comparing the ‘blank,’ or unobstructed, intensity with the measured intensity of the light transmitted through the gas, it is possible to determine the absorption properties of the gas as a function of wavelength, using the Beer-Lambert Law:

\[ I = I_0 e^{-N\sigma(\lambda)} \],

(3.14)

where \( I \) is the measured intensity, \( I_0 \) is the intensity of the background, \( N \) is the column density\(^9\) and \( \sigma(\lambda) \) is the cross section of the molecule as a function of wavelength. The quantity \( N\sigma \) is called the optical depth, \( \tau \), and serves as a measure of gas opacity.

Solving equation 3.14 for the cross section, \( \sigma \), yields,

\[ \sigma(\lambda) = -N \ln \frac{I}{I_0} \].

(3.15)

In order to extract a molecule’s cross section from measured spectra, we must know the

\(^9\)Column density: number of particles per unit area
column density of the gas sample. Current techniques for calculating the vapor composition as a function of temperature are insufficient for determining the $S_2$ column density in our absorption cell. Calibrating the $S_2$ absorption spectrum requires knowing the strength of at least one non-predissociated vibronic transition. In 2011, Shyur and Professor Stark proposed to put the measured spectra on an absolute scale using the absorption strengths from measured spectra and radiative lifetimes from literature to extract the column density indirectly. Isolating the column density from the measured absorption strength of a transition line depends on the oscillator strength of that line and the population of the lower state in the transition. The next sections concentrate on defining oscillator strength and deriving the population distribution of molecules at a given temperature.

3.4.2 Oscillator Strengths and Radiative Lifetimes

The likelihood of a transition’s occurrence characterizes its strength. The probability of a spontaneous optical transition from a higher energy level, $E_i$, to a lower energy level, $E_j$, is given by $A_{ij}\Delta t$. $A_{ij}$, called the Einstein A coefficient, is the transition’s probability per unit time (units: $s^{-1}$) (Griffiths 2005). Calibrating the $S_2$ spectrum requires knowing $A_{\nu',\nu''=0}$ for a single upper state vibrational band, $B(\nu')$.

Einstein A Coefficients

The Einstein A coefficient is related to the **electronic dipole matrix element**, $\mu_{ij}$:

$$A_{ij} = \frac{16\pi^3}{5\varepsilon_0hc^3}\nu^2\mu_{ij}^2$$

(3.16)

---

$^{10}$ The cell and furnace are described in chapter 2 and in more detail in Shyur’s thesis. $^{11}\varepsilon_0$ is the permittivity of free space, $8.85\times10^{-12}$ C²/Nm². $h$ is Planck’s constant, $6.626\times10^{-34}$ Js. $c$ is the speed of light, $3.00\times10^8$ m/s. $\nu$ is the frequency of the transition in Hz.
\( \mu_{ij} \) quantifies the strength of a transition by first operating on the lower state wave function with the electric dipole moment operator, \( \mu(\vec{r}) = \sum e \vec{r} \)\(^{12} \) and then finding its inner product with the upper state wave function:

\[
\mu_{ij} = \left\langle \Psi_i \left| \sum e \vec{r} \right| \Psi_j \right\rangle.
\] (3.17)

In the basis of the Born-Oppenheimer Approximation, the matrix elements become

\[
\mu_{ij} = \left\langle \phi^d_i (r; R) \chi_{i,v'} (R) | \mu(r) | \phi^d_j (r; R) \chi_{j,v''} (R) \right\rangle.
\] (3.18)

Re-expressed in integral form, equation 3.18 is

\[
\mu_{ij} = \int \chi^*_{i,v'} (R) \left[ \int \phi^d_i (r; R) \overrightarrow{\mu(r)} \phi^d_j (r; R) dr \right] \chi_{j,v''} (R) dR.
\] (3.19)

The bracketed term is the electronic transition moment, \( R_e(R) \), of the molecule. It is a function of internuclear separation, \( R \), as are the vibrational wave functions, \( \chi_{i,v} \). Thus, the dipole matrix element may be expressed:

\[
\mu_{ij} = \left\langle \chi_{i,v'} (R) | R_e (R) | \chi_{j,v''} (R) \right\rangle \quad \text{or} \quad \int \chi^*_{i,v'} (R) [R_e (R)] \chi_{j,v''} (R) dR.
\] (3.20)

\( R_e(R) \) is frequently approximated as a constant, allowing it to be removed from the integral:

\[
\mu_{ij} = R_e (R) \left\langle \chi_{i,v'} (R) | \chi_{j,v''} (R) \right\rangle.
\] (3.21)

The quantity, \( \langle \chi_{i,v'} (R) | \chi_{j,v''} (R) \rangle \), is the ‘overlap integral’ between the upper and lower state wave functions. The internuclear separation, \( R \), does not change very much during a transition. Therefore, a transition is most probable if the two wave functions have maxima

\(^{12} \)e is the fundamental charge of an electron, \( 1.60 \times 10^{-19} \) C, and \( \vec{r} \) is the vector position of an electron with respect to the origin of the chosen coordinate system.
around the same value of $R$. The square of the overlap integral yields the **Franck-Condon factor**, $q_{v',v''} = |\langle \Psi_{i,v'} | \Psi_{j,v''} \rangle|^2$. The sum of the Franck-Condon factors is 1, $\sum_{v''} q_{v',v''} = 1$, because any wave function, $|\Psi\rangle$, can be expressed as a linear combination of a basis set of wave functions, $|\phi_n\rangle$, weighted by projection coefficients $c_n$. Since all wave functions must be normalized, the projection coefficients must sum to 1:

$$\sum_n |c_n|^2 = \sum_n |\langle \phi_n | \Psi \rangle|^2 = 1.$$  \hspace{1cm} (3.22)

Franck-Condon factors are also projections of $\Psi_{i,v'}$ onto the assorted $\Psi_{j,v''}$, and therefore also sum to 1 (Shyur 2011; Griffiths 2005).

**Oscillator Strengths**

Unitless oscillator strengths, or ‘f-values,’ are proportional to Einstein A coefficients:

$$f_{ij} = \frac{\varepsilon_0 mc^3}{2\pi e^2 \nu^2} A_{ij}.$$  \hspace{1cm} (3.23)

The f-value of a whole vibrational band, $f_{v',v''} \propto A_{v',v''}$, called a ‘band f-value,’ is related to the integrated laboratory cross section, $\sigma(\lambda)$, discussed in section 3.4.1:

$$\int_{\text{band}} \sigma (\lambda) \, d\lambda = \frac{e^2}{4\varepsilon_0 mc} f_{\text{band}}.$$  \hspace{1cm} (3.24)

If we can isolate $A_{v',v''=0}$ to find the molecule’s integrated cross section, and, from there, calibrate the column density, N, using the Beer-Lambert law (equation 3.14). Calculating $A_{v',v''=0}$ requires that we manipulate the equations for radiative lifetime (Shyur 2011).
**Radiative Lifetimes**

The radiative lifetime of an upper energy level is approximately the average amount of time an electron will spend in that energy level before decaying to a lower level. The radiative lifetime of an energy level with a single decay channel \( i \rightarrow j \) is the inverse of its Einstein A coefficient, \( \tau = \frac{1}{A_{ij}} \).

However, most excited states have multiple decay channels. The lifetime of the state shortens when more available decay routes exist. The lifetime is the inverse sum of the Einstein A coefficients for all possible decay routes, \( \tau = \frac{1}{\sum_j A_{ij}} \) (Griffiths 2005). We call these decay paths transitions. Einstein A coefficients are the probability per unit time for transitions occurring solely by radiative processes. Thus, this calculation for lifetime must be modified if decay processes other than radiation exist. One such process is predissociation.

To calculate the lifetime of a predissociating state (discussed in section 3.3.2), the predissociation rate must be included:

\[
\tau = \frac{1}{\sum_j A_{ij} + A_{iPD}}. \tag{3.25}
\]

The predissociation decay channel shortens the lifetime of an upper state substantially, since \( A_{iPD} \) is large compared to the radiative probability, \( \sum_j A_{ij} \). Shortened lifetimes are responsible for broadened absorption features.

Einstein A coefficients serve as a bridge between radiative lifetimes and oscillator strengths. Oscillator strengths can be used to find the integrated cross section, \( \int_{\text{band}} \sigma (\lambda) \, d\lambda \) (related to the cross section by optical depth, see equation 3.14) (Archer 2012, Shyur 2011).

Radiative lifetimes can be measured in the laboratory, and such measurements have been made for \( S_2 \) (Wheeler et al. 1998; Green & Western 1996; Matsumi et al. 1985). However, the predissociation probabilities for the upper vibrational levels of the B state are
unknown. As a result, we cannot extract $A_{v',v''=0}$ for the upper levels. We must choose low-lying vibrational bands for our column density calibration.

**Extracting $A_{v',v''=0}$ from Known Radiative Lifetimes**

![Diagram of energy level transitions](image)

*Figure 3.7: Each decay channel has an Einstein A coefficient.*

$A_{v',v''=0}$ connects radiative lifetimes for transitions from a given vibrational level of the excited B state to the ground vibrational level of the X state to their band f-values. Equation 3.16 relates Einstein A coefficients and dipole matrix elements for non-predissociating levels. $A_{v',v''}$ and $A_{v',v''=0}$ are proportional to:

$$A_{v',v''} \propto \nu_{v',v''} \mu_{v',v''}^2$$  \hspace{1cm} (3.26)

$$A_{v',0} \propto \nu_{v',0} \mu_{v',0}^2.$$  \hspace{1cm} (3.27)

Therefore,

$$A_{v',v''} = A_{v',0} \left( \frac{\nu_{v',v''}}{\nu_{v',0}} \right)^3 \left( \frac{\mu_{v',v''}}{\mu_{v',0}} \right)^2.$$  \hspace{1cm} (3.28)

Summing both sides of equation 3.28 over all $v''$ gives

$$\sum_{v''} A_{v',v''} = \sum_{v''} A_{v',0} \left( \frac{\nu_{v',v''}}{\nu_{v',0}} \right)^3 \left( \frac{\mu_{v',v''}}{\mu_{v',0}} \right)^2 = \frac{A_{v',0}}{\nu_{v',0}^3 \mu_{v',0}^2} \sum_{v''} \nu_{v',v''}^3 \mu_{v',v''}^2.$$  \hspace{1cm} (3.29)
The radiative lifetime, $\tau$, of an upper state is one over the sum of the Einstein A coefficients of all possible decay channels (figure 3.7). Thus, we can make the substitution $\tau = \frac{1}{\sum_{\nu''} A_{\nu',\nu''}}$, so that equation 3.29 simplifies to

$$\frac{1}{\tau} = \frac{A_{\nu',0}}{\nu_{\nu',0}^3 \mu_{\nu',0}^2} \sum_{\nu''} \nu_{\nu',\nu''}^3 \mu_{\nu',\nu''}^2.$$  (3.30)

Solving equation 3.30 for $A_{\nu',0}$ gives us the band Einstein A coefficient:

$$A_{\nu',0} = \frac{\nu_{\nu',0}^3 \mu_{\nu',0}^2}{\tau} \frac{1}{\sum_{\nu''} \nu_{\nu',\nu''}^3 \mu_{\nu',\nu''}^2}.$$  (3.31)

Now we can calculate the band f-values using equation 3.23. The column density is proportional to the measured line strength divided by the band f-value (Shyur 2011). The dipole matrix elements, $\mu_{\nu',\nu''}$, will be determined using the dipole transition moment in literature (Pradhan & Partridge 1996; Kiljunen et al. 2000) and equation 3.20. In S$_2$, the vibrational bands are overlapped, so it is not possible to measure the strength of a single band. Instead, we must use individual rotational lines within each band.

### 3.4.3 Rotational Line Strength and Hund’s Cases

The column density is inversely proportional to the rotational line strength of a transition, called the Hönl-London factor, $HL$.

Hönl-London factors weight the strength of rotational lines within the same vibrational band. Rephrased, they are proportional to the probability of a given rotational transition. The line f-value, $f_l$, of a transition is directly proportional to the band f-value:

$$f_l = (HL) f_b.$$  (3.32)

Each branch of transitions (section 3.3.3) has its own set of J-dependent Hönl-London factors.
We are extracting the column density from individual, measured rotational lines within each vibrational band. To extract the column density from the measured line strength, the line’s transition branch must be known (and thus, its associated $HL$ factor), in addition to its vibrational band, $(v'-v'')$, and its lower state total angular momentum quantum number, $J''$.

**Hund’s Cases**

The set of Hönl-London factors appropriate for an electronic transition (e.g. the B-X transition) is determined by Hund’s Cases. There are many Hund’s Cases covering the variation in molecular structure. This discussion concentrates on cases (a) and (b).

In using the Born-Oppenheimer approximation (section 3.1), we have partitioned the full molecular Hamiltonian (equation 3.1) into its diagonal and off-diagonal terms. This section provides a brief overview of the treatment for the rotational off-diagonal terms. For further information, please consult Lefebvre-Brion & Field 2004 or Bernath 1995.

The rotational Hamiltonian, $H_{\text{rot}}$ in equation 3.1, describes the rotational energy of the nuclei:

$$H_{\text{rot}} = \left( \frac{1}{2\mu R^2} \right) \overrightarrow{R} \cdot \overrightarrow{R} = \left( \frac{1}{2\mu R^2} \right) R^2.$$  (3.33)

where $\overrightarrow{R}$ is the rotational angular momentum operator and $R$ is the internuclear separation. The rotational angular momentum of the nuclei is always perpendicular to the internuclear axis, thus its $z$-component is zero. Accounting for this, the rotational Hamiltonian is:

$$H_{\text{rot}} = \left( \frac{1}{2\mu R^2} \right) (R_x^2 + R_y^2).$$  (3.34)

Using $\overrightarrow{R} = \overrightarrow{J} - \overrightarrow{L} - \overrightarrow{S}$ and raising and lowering operators, we can express equation 3.34 in terms of the operators $J^2, J_z, S^2, S_z, L_z$ and the raising and lowering operators of $\overrightarrow{J}, \overrightarrow{L}$,

$\overrightarrow{J}$ is the total angular momentum operator, $\overrightarrow{L}$ is the orbital angular momentum operator, and $\overrightarrow{S}$ is the intrinsic angular momentum (spin) operator.
and \( \vec{S} \).

\( H^{\text{rot}} \) is not diagonal in any simple basis when the intrinsic quantum number, \( S \), is not 0. A relativistic term in the full molecular Hamiltonian, called the spin-orbit Hamiltonian, also contains off-diagonal terms in most bases. Hund’s cases help us select the basis with the smallest off-diagonal terms when the rotational and spin-orbit terms are included in the analysis. Cases (a) and (b) are briefly considered here, with further details available in Lefebvre-Brion & Field 2004 or Bernath 1995. For each basis, we divide the full Hamiltonian into its diagonal elements, \( H^{(0)} \), and off-diagonal elements, \( H^{(1)} \). We select a case based on the relative sizes of the terms in the Hamiltonian:

<table>
<thead>
<tr>
<th>Hund’s Case</th>
<th>( H^{el} )</th>
<th>( H^{SO} )</th>
<th>( H^{rot} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>strong</td>
<td>intermediate</td>
<td>weak</td>
</tr>
<tr>
<td>b</td>
<td>strong</td>
<td>weak</td>
<td>intermediate</td>
</tr>
</tbody>
</table>

The electronic Hamiltonian, \( H^{el} \), is much stronger than the other terms - it is always included in \( H^{(0)} \). \( H^{SO} \) and \( H^{rot} \) are divided according to the cases. In case (a), the spin-orbit terms exceed the rotational terms. This case works well when the total angular momentum quantum number, \( J \), is small. In case (b), the rotational terms are larger than the spin-orbit terms - in other words, in the high-\( J \) limit. As such, the choice of appropriate basis tends to evolve from case (a) to (b) as we move to higher \( J \).

**Hund’s Case (a)**

In Hund’s case (a), the spin-orbit terms in the Hamiltonian are greater than the rotational terms. \( H^{(0)} \) includes \( H^{el} \) and the diagonal elements of \( H^{rot} \). The spin-orbit terms, \( H^{SO} \), and off-diagonal terms of \( H^{rot} \) form \( H^{(1)} \). This basis consists of the eigenfunctions of operators \( J^2, J_z, S^2, S_z \), and \( L_z \) with good quantum numbers \( J, \Omega, S, \Sigma, \) and \( \Lambda \).

The diagonal, or ‘zero-order,’ energies are \( B \{ J (J + 1) - \Omega^2 + S (S + 1) - \Sigma^2 \} \), where \( B \) is the rotational constant. For a given energy level with \( E \approx BJ(J+1) \), there are \( 2S+1 \) states. Consider the example of a triplet sigma state, \( ^3\Sigma_{-1,0,1} \):
There are three distinct ladders of rotational states, labelled by $\Omega$, with pattern-forming quantum number $J$.

**Hund’s Case (b)**

In Hund’s case (b), the rotational terms in the full Hamiltonian are larger than the spin-orbit terms. As such, we divide the Hamiltonian differently in case (b) to minimize the off-diagonal matrix elements. Using the relationship $N = J - S = L + R$, we re-express $H^{\text{rot}}$ in terms of $N$. Once recast, $H^{(0)}$ consists of $H^{el}$ and the diagonal portion of $H^{\text{rot}}$, expressed in terms of $N$. The zero-order energies are $B \left\{ N(N + 1) - \Lambda^2 \right\}$.

In case (b), there are $BN(N + 1)$ distinct energy levels. Spin results in $2S + 1$ states within each energy level (for each value of $N$). Since $J = N + S$, $J$ ranges from $N + S$ to $|N - S|$. In a triplet sigma state where $S = 1$, $J$ can only be 1 when $N = 0$. $N$ is the pattern forming quantum number in case (b).

**Figure 3.8: Zero-order energy level structure for Hund’s cases (a) and (b) for $^3\Sigma$ states**
Hund’s cases allow us to describe limiting cases for the energy-level patterns. Like most molecular systems, the B-X system in S\(_2\) is intermediate between cases (a) and (b). Tatum & Watson 1971 provide a table of the 14 H"onl-London factors corresponding to the 14 branches of \(^{3}\Sigma - ^{3}\Sigma\) transitions whose states are intermediate between cases (a) and (b).

### 3.4.4 Population Distribution

The column density is also inversely proportional to the relative population of the lower state’s rotational level compared to other lower state rotational levels. The Boltzmann factor, \(Boltz\), is a statistical weighting factor that determines the relative probability of a system in a particular state, compared to all of its other possible states, in thermodynamic equilibrium. We can use the Boltzmann factor to determine the relative populations in the rotational levels of a vibrational band,

\[
Boltz(J'') = \frac{(2J'' + 1)e^{-\frac{E(J'')}{k_bT}}}{\sum_{J''=0}^{\infty} (2J'' + 1)e^{-\frac{E(J'')}{k_bT}}}.
\]

\(J''\) is the rotational quantum number of the lower state. \(E(J'')\) is the energy of the state \(X(v'',J'')\). \(k_b\) is the Boltzmann Constant, \(1.38 \times 10^{-23}\) J/K, and \(T\) is the temperature of the gas molecules in Kelvin. Figure 3.9 compares the modeled vibrational band of a singlet-singlet \((^{1}\Sigma,^{1}\Sigma)\) transition spectrum at room temperature (295 K) and at high temperature (1000 K). The high temperature thermally populates higher rotational levels in the vibrational band, producing more rotational transitions. The models were generated using PGopher\(^\text{14}\). S\(_2\) constants from Huber & Herzberg 1979 were used for both models.

\(\text{http://pgopher.chm.bris.ac.uk}\)

\(^{14}\text{PGOPHER, a Program for Simulating Rotational Structure, C. M. Western, University of Bristol,}\)
(a) Singlet-Singlet vibrational band at room temperature (295 K), modeled in PGopher

(b) Singlet-Singlet vibrational band at high temperature (1000 K), modeled in PGopher

*Figure 3.9:* Comparing spectra at room temperature and high temperature
3.4.5 The Column Density Equation

This section formally relates the column density calibration to the band f-values and measured transition line strengths. Chapter 4 presents the column density measurement, calculated by this approach, for one spectrum from the January 2014 run.

The measured line strength, $S$, is its integrated optical depth, $\tau$. Section 3.4.1 explained that $\tau$ is the gas column density multiplied by its molecular cross section, $\sigma(\lambda)$. Thus,

$$S = \int_{\text{line}} \tau(\lambda) d\lambda = \int_{\text{line}} N\sigma(\lambda) d\lambda.$$  \hspace{1cm} (3.36)

The column density, $N$, is a constant and so can be pulled out of the integral. Solving for $N$ gives,

$$N = \frac{S}{\int_{\text{line}} \sigma(\lambda) d\lambda}. \hspace{1cm} (3.37)$$

The integrated cross section of a line, $\int_{\text{line}} \sigma(\lambda) d\lambda$, is related to that line’s f-value, $f_l$,

$$f_l = (1.13 \times 10^{12}) \int_{\text{line}} \sigma(\lambda) d\lambda \cdot \frac{Boltz}{\text{J}}.$$ \hspace{1cm} (3.38)

where $Boltz$ is the Boltzmann factor. Plugging $f_l$ into equation 3.37 gives,

$$N = \frac{(1.13 \times 10^{12}) S}{Boltz \cdot f_l}. \hspace{1cm} (3.39)$$

However, we can only isolate band f-values from measured radiative lifetimes. The line f-value is related to the band f-value of the line’s vibrational band by the HönL-London factor, $HL$, corresponding to that transition line’s branch. Replacing $f_l$ in equation 3.39 with $HL \cdot f_{band}$ yields the column density calibration equation:

$$N = \frac{(1.13 \times 10^{12}) S}{Boltz \cdot HL \cdot f_{band}}. \hspace{1cm} (3.40)$$
Chapter 4

Results and Discussion

This chapter seeks to apply the results of the theoretical discussion in chapter 3 to calibrate the column density of a January 2014 spectrum collected at NIST.

4.1 Presentation of Spectra

Table 2.5 lists the measurements made in January 2014 at NIST, which constitute our final data set. Under each set of conditions, we collected spectra simultaneously using the FTS’ dual output mode in the spectral ranges shown in figure 2.17. Spectra are referred to according to their measured side-arm temperature. Figure 4.1 displays the collected spectra from both spectral ranges at a side-arm temperature of 130°C. The other spectra are in appendix D.

The predissociated bands are clearly visible in figure 4.1(a). The rotational structure is evident in figure 4.1(b). The two band passes overlap from about 32,000 cm\(^{-1}\) to 40,000 cm\(^{-1}\), allowing examination of both the rotational and predissociated structure in either band pass. Comparing figures [D.1(a), 4.1(a), D.2(a), D.3(a), D.4(a) & D.6(a), D.5(a) & D.7(a)] and [D.8(a)] indicates continuum absorption by S\(_2\) above approximately 40,100 cm\(^{-1}\).
Figure 4.1: Spectra: 130°C side-arm temperature, 550°C absorption cell temperature. The background spectrum is red; the absorption spectrum is black.
4.2 Measured Optical Depth

Optical depth is the gas column density multiplied by its molecular cross section. The cross is a property of the molecule - the column density serves as a scale factor.

By plotting the measured optical depth of all the collected spectra as a function of wavenumber on a single figure (figure 4.2), we can observe the scaling effects of the column density. We expect the shape of each optical depth curve to be a constant function multiplied by a scale factor.

Determining the optical depth requires solving the Beer-Lambert law for the expo-
component, \( \tau = N\sigma \) (see section 3.4.1). Each spectrum consists of the measured intensity, \( I \), while the blanks serve as \( I_0 \).

The blank must first be modified to minimize noise and account for drift in intensity over the course of the day.\(^1\) The blank is essentially featureless, and therefore oversampled at our resolution. It was smoothed to reduce noise using the running average function in the plotting routine \( \text{xmgrace} \)\(^2\) over 5000 points. The smoothing process averaged the Xe emission peaks into the blanks. Since the emission peaks still exist in the experimental spectra, they had to be artificially restored to the blanks, using a program coded in MATLAB.

Over the course of a day, sulfur can deposit on the absorption cell windows, reducing transmission. As a result, the true background of an absorption scan may differ compared to the original background scan, recorded at the beginning of the day. Figure 4.3(a) shows an original (unmodified) background scan and absorption scan. Figure 4.3(b) shows that multiplying the background by a constant to match one side of the absorption scan fails to match the other side. The obstructive presence of sulfur on the cell windows has a greater effect at shorter wavelengths. Figure 4.3(c) illustrates that we can adjust the background effectively to accommodate this effect by multiplying the background by a linear function:

\[
I_0 = I_{\text{blank}} \left( b (x - x_0) + a \right),
\]

where \( b \) is the change in multiplier measured at two specified wavenumbers divided by the difference in the specified wave numbers. \( a \) is the multiplier at the first wavenumber (starting wavenumber) in the blank. \( x \) is the current wavenumber and \( x_0 \) is the starting wavenumber. The multipliers were found by adjusting the blank relative to each absorption scan in

\(^1\)For each spectrum, we must determine the true background intensity. Over the course of the day, the intensity of the lamp can drift in both profile and intensity. Ordinarily, we set the true background by averaging blanks taken immediately before and after each scan. But, that is not possible with the S\(_2\) measurements. We aim to replicate the true background of the spectrum by multiplying by a linear function.

Figure 4.3: Adjusting the measured background to find the true background
xmgrace. We used the hot blanks (table 2.5), taken at 500°C prior to the presence of \( \text{S}_2 \) vapor. The blank matching the date of the absorption spectrum was used. Tables 4.1 and 4.2 compile the multipliers for every measurement in each spectral range. All multipliers have an uncertainty of ± 0.005.

<table>
<thead>
<tr>
<th>UV/Solar Blind</th>
<th>Day 1</th>
<th>Multipliers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Intercept (32500 cm(^{-1}))</td>
<td>Low (32500 cm(^{-1}))</td>
</tr>
<tr>
<td>120</td>
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<td>1.34</td>
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<tr>
<td>175</td>
<td>0.85</td>
<td>0.85</td>
</tr>
<tr>
<td>195</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>Day 2</td>
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<td></td>
</tr>
<tr>
<td>175</td>
<td>1.17</td>
<td>1.17</td>
</tr>
<tr>
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</tr>
<tr>
<td>215</td>
<td>1</td>
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</tr>
</tbody>
</table>

*Table 4.1: Multipliers for the UV/Solar Blind spectral range blanks for each measurement*

<table>
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<th>Multipliers</th>
</tr>
</thead>
<tbody>
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<td>Low (25775 cm(^{-1}))</td>
</tr>
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<tr>
<td>175</td>
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<td>0.722</td>
</tr>
<tr>
<td>195</td>
<td>0.615</td>
<td>0.601</td>
</tr>
<tr>
<td>Day 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>175</td>
<td>1.19</td>
<td>1.175</td>
</tr>
<tr>
<td>195</td>
<td>0.85</td>
<td>0.84</td>
</tr>
<tr>
<td>215</td>
<td>1.183</td>
<td>1.16</td>
</tr>
</tbody>
</table>

*Table 4.2: Multipliers for the UV-visible spectral range blanks for each measurement*

A python program, `Tau.py`, was written to correct for the drift in the blank and calculate the measured optical depth for the specified scans. The user inputs the filename of both the blank and the absorption scan and supplies the appropriate multipliers from tables 4.1 and 4.2. `Tau.py` output two files - one containing the corrected \( I_0 \) and another
containing the measured optical depth as a function of wave number. Figure 4.2 plots the optical depth as a function of wavenumber for the January measurements. They appear to reflect a single function (interpreted as the $S_2$ cross section) multiplied by a scaling factor (the column density). This suggests a stable column density at each temperature. A copy of \texttt{Tau.py} is available in appendix E.

4.3 Extracting the Column Density for the 130°C Measurements

In order to determine the column density of a single spectrum, we must perform the following routine:

1. Select reliable, identifiable spectral lines within one vibrational band
2. Measure the line strength of each line using a fitting routine
3. Analyze the measured relative strength of each line to extract its column density using equation 3.40 (derived in section 3.4.5)
4. Perform a weighted average of the individual column densities to find an average column density for the spectrum.

In principle, this process should be repeated across several low-lying vibrational bands\textsuperscript{3} in order to ensure a reliable column density calibration. This work presents an estimate for one spectrum based on a single vibrational band. We focused on the $(v' = 4, v'' = 0)$ band at 130°C. We worked in the UV-visible spectral range because the response of this detector-filter combination was more effective in the low-lying vibrational bands in this spectral range than that of the UV/Solar blind combination.

\textsuperscript{3}We cannot use upper vibrational bands since they are strongly perturbed by interactions with the $B''$ state.
4.3.1 Identifying Reliable Spectral Lines

Using equation 3.40 for the column density requires interpreting the strength of individual lines. The total strength of a blended absorption feature is the sum of the individual strengths of all its constituent lines. It is difficult to reliably isolate the strength of an individual line from the composite. For this reason, we selected single-line absorption features.

In addition, in order to use equation 3.40, we must be able to identify the line in the feature by its lower state rotational quantum number, $J''$, and transition branch so that we can calculate its Boltzmann factor and Hönl-London factor.

Most of the Hönl-London factors, presented in Tatum & Watson, depend on both the lower and upper state constants of the molecule. The upper state constants for S$_2$ are poorly known, introducing additional uncertainty in the Hönl-London factors of transition branches requiring those constants. Four of the 14 branches have Hönl-London factors independent of the upper state constants: $^P P_{2,2}$, $^R R_{2,2}$, $^P Q_{2,3}$, and $^R Q_{2,1}$. Of these, $^P Q_{2,3}$ and $^R Q_{2,1}$ are weaker satellite branches, and therefore more difficult to identify in the experimental spectrum. Thus, we concentrated on lines from the strong $^P P_{2,2}$ and $^R R_{2,2}$ branches.

Finally, the calculation of $f_{band}$, required for equation 3.40, ignores the effects of the perturbing B$''$ state. In the low-lying vibrational bands, the B$''$ interaction serves to increase the stability of the excited state, thus increasing its lifetime and decreasing the overall strength of the transition. We need to choose pure B-X transition lines, distinguishable from perturbed lines by their lifetimes. A typical ‘pure’ B-X transition in S$_2$ has a lifetime of approximately 32 ns (Wheeler et al. 1998; Green & Western 1996; Matsumi et al. 1984).

In summary, chosen absorption features must be:

1. Single-line features
2. From the $^P P_{2,2}$ or $^R R_{2,2}$ branches
3. Unperturbed (approximately 32 ns lifetime)

C.M. Western of the University of Bristol kindly supplied us with a line list identifying B-X and B''-X transitions in S\textsubscript{2}, by their transition energy, branch and rotational quantum numbers, and lifetime. The list provides identifications for transitions from B(v' = 0-6) to X(v'' = 0), including the (4,0) band (Green & Western 1996). We compared the listed lines to our spectrum to identify candidate lines. We anticipated approximately 40 useable lines in the (4,0) vibrational band, based on the reported lifetimes. Only six lines met all our criteria. In the future, these criteria may have to be relaxed.

4.3.2 Line Fitting

In order to measure the relative strength, \( S \), of a line, we use a fitting program developed by Dr. Alan Heays of Leiden Observatory. The program interactively refines user specified parameters to fit a measured absorption spectrum. The program runs a command file containing the spectrum to be processed, specifications of the molecule in question, and the initial parameters. In the command file, the user specifies the energy range corresponding to the portion of the spectrum to be fit and provides estimates for the position, relative strength, and line width of each absorption feature present in that energy range. The user also indicates which of those parameters (position, strength, and width) the program may vary, if any. Additionally, the user must enter the width of instrument function, corresponding to the instrument resolution (see section 2.3).

The program manipulates the initial parameters to produce a theoretical spectrum. For each absorption feature, the program prepares a ‘true’ spectrum, called a Voigt profile, consisting of the Gaussian-shaped thermal Doppler width and the natural line width - related to the radiative lifetime\(^4\) and represented by a Lorentzian. Then, it convolves the

\[^4\text{Line width, } \Gamma = \frac{1}{2\pi c \tau}, \text{ where } c \text{ is the speed of light and } \tau \text{ is the lifetime.}\]
true spectrum with the instrument function to produce the spectrum measured by the instrument. The program sums the simulated spectra of all the absorption features to get the full measured spectrum in the energy interval specified. Then, it iteratively improves the parameters of the generated spectrum to replicate the experimental spectrum. When the fit can no longer be improved, the program saves an output file containing the final parameters for each feature (position, strength, and width) and their errors, as well as the measured spectrum. Figure 4.4 displays the fit for one group of S\textsubscript{2} lines used in the column density calibration.

4.3.3 Applying the Column Density Equation

To apply the column density equation (equation 3.40), we must calculate the rotational Boltzmann factors, f-values, and transition frequencies. These calculations were performed
Calculating Boltzmann Factors

First, we calculated the rotational energy levels of the electronic ground state-vibrational ground state energies of \( S_2 \) (X, \( v = 0 \)) for multiple values of \( J'' \) by diagonalizing the Hamiltonian matrix given in Amiot et al. 1981 using lower state constants from Fink et al. 1986. Next, we calculated the Boltzmann factors for \( J'' \) at 550°C, the absorption cell temperature of our spectrum, using equation 3.35.

Calculating f-values

Calculating the f-values requires calculating both the vibrational band energies (using equation 3.13 without the rotational terms) and the electric dipole matrix elements (equation 3.20). The vibrational transition energies of the first ten levels and the 40th are given in table 4.3.

To calculate the electric dipole matrix elements, we generated wave functions for \( \nu'' = 0-40 \) and \( \nu' = 0-6 \) using Dr. Gibson’s CSE program. The CSE program requires the potential energy curve of the electronic state of interest. We used Dr. Gibson’s RKR program to generate the X and B potential energy curves. We used measured vibrational energy levels and rotational constants from Green & Western 1996 for the X state and B state. Dr. Gibson fit the \( S_2 \) transition moment from Pradhan & Partridge 1996. Figure 4.5 illustrates the agreement in transition moment between Dr. Gibson and Pradhan & Partridge, as well as a second source from Kiljunen et al. 2000. A program written in MATLAB calculated the matrix elements, according to equation 3.20.
Another MATLAB program performed equation 3.23, by way of equation 3.16, to calculate the f-values from the vibrational transition frequencies (in Hz) and dipole matrix elements. The lifetime of all transitions was taken as 32 ns in this calculation (Wheeler et al. 1998; Green & Western 1996; Matsumi et al. 1985). Our calculated f-values agree well with Shyur’s 2011 results. Plot 4.6 visually compares our calculated f-values for (4,v′′) with those calculated by Shyur and the theoretical predictions made by Pradhan & Partridge. Table 4.4 tabulates our calculated f-values for v′ = 0 - 6 and v″ = 0 - 20. Key for the column density calculation, \( f_{\text{band}} \) for (4,0) is \( 1.1 \times 10^{-3} \).
Table 4.3: Vibrational B-X transition energies in S₂ (cm⁻¹)

<table>
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<th>( v' \rightarrow )</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tr>
<td>( v'' \downarrow )</td>
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<td></td>
<td></td>
<td></td>
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Figure 4.6: f-values for \((4, v'')\)
### Table 4.4: Calculated $S_2$ B-X $f$-values, no perturbations considered ($\times 10^{-3}$)

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<th>$v' = 0$</th>
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<td>7.60</td>
<td>5.04</td>
<td>1.65</td>
<td>0.0192</td>
</tr>
<tr>
<td>$v'' = 4$</td>
<td>2.10</td>
<td>6.26</td>
<td>7.76</td>
<td>4.26</td>
<td>0.503</td>
<td>0.498</td>
<td>2.87</td>
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<tr>
<td>$v'' = 5$</td>
<td>4.08</td>
<td>7.93</td>
<td>4.96</td>
<td>0.370</td>
<td>1.11</td>
<td>3.97</td>
<td>3.72</td>
</tr>
<tr>
<td>$v'' = 6$</td>
<td>6.51</td>
<td>7.17</td>
<td>1.12</td>
<td>0.935</td>
<td>4.10</td>
<td>2.99</td>
<td>0.255</td>
</tr>
<tr>
<td>$v'' = 7$</td>
<td>8.89</td>
<td>4.25</td>
<td>0.137</td>
<td>3.88</td>
<td>2.93</td>
<td>0.0555</td>
<td>1.51</td>
</tr>
<tr>
<td>$v'' = 8$</td>
<td>10.4</td>
<td>1.04</td>
<td>2.62</td>
<td>3.83</td>
<td>0.125</td>
<td>1.79</td>
<td>3.17</td>
</tr>
<tr>
<td>$v'' = 9$</td>
<td>10.2</td>
<td>0.0731</td>
<td>4.97</td>
<td>0.852</td>
<td>1.42</td>
<td>3.28</td>
<td>0.520</td>
</tr>
<tr>
<td>$v'' = 10$</td>
<td>8.16</td>
<td>2.20</td>
<td>3.77</td>
<td>0.345</td>
<td>3.63</td>
<td>0.722</td>
<td>0.888</td>
</tr>
<tr>
<td>$v'' = 11$</td>
<td>5.46</td>
<td>5.37</td>
<td>0.831</td>
<td>3.07</td>
<td>1.81</td>
<td>0.567</td>
<td>2.91</td>
</tr>
<tr>
<td>$v'' = 12$</td>
<td>3.15</td>
<td>7.04</td>
<td>0.181</td>
<td>4.03</td>
<td>0.0047</td>
<td>3.07</td>
<td>0.909</td>
</tr>
<tr>
<td>$v'' = 13$</td>
<td>1.58</td>
<td>6.41</td>
<td>2.54</td>
<td>1.68</td>
<td>2.00</td>
<td>2.03</td>
<td>0.377</td>
</tr>
<tr>
<td>$v'' = 14$</td>
<td>0.689</td>
<td>4.48</td>
<td>5.19</td>
<td>0.000622</td>
<td>3.65</td>
<td>0.00608</td>
<td>2.72</td>
</tr>
<tr>
<td>$v'' = 15$</td>
<td>0.257</td>
<td>2.53</td>
<td>5.84</td>
<td>1.53</td>
<td>1.85</td>
<td>1.70</td>
<td>1.76</td>
</tr>
<tr>
<td>$v'' = 16$</td>
<td>0.0794</td>
<td>1.17</td>
<td>4.56</td>
<td>4.21</td>
<td>0.0195</td>
<td>3.33</td>
<td>0.000814</td>
</tr>
<tr>
<td>$v'' = 17$</td>
<td>0.0206</td>
<td>0.443</td>
<td>2.71</td>
<td>5.24</td>
<td>1.27</td>
<td>1.60</td>
<td>1.80</td>
</tr>
<tr>
<td>$v'' = 18$</td>
<td>0.00469</td>
<td>0.136</td>
<td>1.26</td>
<td>4.26</td>
<td>3.82</td>
<td>0.0016</td>
<td>2.99</td>
</tr>
<tr>
<td>$v'' = 19$</td>
<td>0.000949</td>
<td>0.0349</td>
<td>0.464</td>
<td>2.53</td>
<td>4.80</td>
<td>1.42</td>
<td>1.09</td>
</tr>
<tr>
<td>$v'' = 20$</td>
<td>0.000144</td>
<td>0.00772</td>
<td>0.140</td>
<td>1.14</td>
<td>3.82</td>
<td>3.77</td>
<td>0.0437</td>
</tr>
</tbody>
</table>

**Calculating Hönl-London Factors**

The Hönl-London factors, $HL$, for a given $J''$ and transition branch were calculated in MATLAB using the expressions in Tatum & Watson 1971. Finally, a MATLAB program calculated the column density from equation 3.40 for a given transition line. It requires $S$, $Boltz$, $HL$, and $f_{band}$. 
4.3.4 The Column Density of the 130°C Spectrum

Figure 4.7: Column density estimate for 130°C spectrum

Table 4.5 records the six qualifying lines according to the criteria in section 4.3.1. For each line, its transition energy, branch, rotational quantum number $J''$, Boltzmann factor $Boltz$, Hönl-London factor $HL$, lifetime (according to Green & Western 1996), measured strength $S$ and fractional error in measured strength, its estimate for the column density, $N$, and the error in $N$ are given.

Figure 4.7 plots the column density (cm$^{-1}$), $N$, versus transition energy (cm$^{-1}$) for each line. Taking a weighted average, as described in Taylor 1997, of all lines gives the column density estimate for 130°C: $N = (4.3 \pm 0.3) \times 10^{15}$ cm$^{-2}$. This uncertainty in the column density of less than 10% appears sufficient. However, this estimate needs to be repeated across multiple bands. Hopefully, multiple bands agree on the column density to within 10%. If not, this may indicate systemic errors in our measurements. Given this column density estimate for the 130b spectrum, the cross section of S$_2$ is shown in figure 4.8.
Further work includes improving the precision of this column density calibration and calibrating the other scans. Once all scans are calibrated, it will be possible to extract the molecular cross sections of diatomic sulfur.
<table>
<thead>
<tr>
<th>Energy (cm(^{-1}))</th>
<th>Branch</th>
<th>J’</th>
<th>Boltz</th>
<th>HL</th>
<th>Lifetime (s)</th>
<th>S</th>
<th>Fractional Strength Error</th>
<th>N (cm(^{-2}))</th>
<th>ΔN ((×10^{15}) cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>33327.0</td>
<td>R2</td>
<td>21</td>
<td>9.69×10(^{-3})</td>
<td>0.511</td>
<td>3.29E-08</td>
<td>0.019</td>
<td>0.168</td>
<td>4.06E+15</td>
<td>0.682</td>
</tr>
<tr>
<td>33337.7</td>
<td>R2</td>
<td>17</td>
<td>8.55×10(^{-3})</td>
<td>0.513</td>
<td>3.28E-08</td>
<td>0.017</td>
<td>0.110</td>
<td>4.05E+15</td>
<td>0.446</td>
</tr>
<tr>
<td>33338.9</td>
<td>P2</td>
<td>11</td>
<td>6.14×10(^{-3})</td>
<td>0.474</td>
<td>3.27E-08</td>
<td>0.011</td>
<td>0.171</td>
<td>3.73E+15</td>
<td>0.638</td>
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<tr>
<td>33342.0</td>
<td>R2</td>
<td>15</td>
<td>7.84×10(^{-3})</td>
<td>0.514</td>
<td>3.27E-08</td>
<td>0.019</td>
<td>0.180</td>
<td>4.82E+15</td>
<td>0.868</td>
</tr>
<tr>
<td>33346.6</td>
<td>P2</td>
<td>7</td>
<td>4.17×10(^{-3})</td>
<td>0.457</td>
<td>3.27E-08</td>
<td>0.011</td>
<td>0.151</td>
<td>6.10E+15</td>
<td>0.911</td>
</tr>
<tr>
<td>33348.8</td>
<td>R2</td>
<td>11</td>
<td>6.15×10(^{-3})</td>
<td>0.518</td>
<td>3.27E-08</td>
<td>0.014</td>
<td>0.528</td>
<td>4.55E+15</td>
<td>2.40</td>
</tr>
</tbody>
</table>

*Table 4.5: (4,0) lines used in column density calibration*
Bibliography


This work is dedicated to my grandfather, Eugene Herde, and my aunt, Susanna Dennis.
Appendix A

Verifying the Solution of the Adiabatic Born-Oppenheimer Approximation for a Simple System

The adiabatic treatment of the molecular Hamiltonian presented in section 3.1 can be verified by assessing the true molecular wave function, $\Psi(r, R) = \psi_{el}(r; R)\psi_N(R)$, for a molecule with two nuclei and one electron, like $H_2^-$, under the influence of the adiabatic Born-Oppenheimer Approximation. The position of each nucleus with respect to the origin of the chosen coordinate system is $R_\alpha$ where $\alpha = 1, 2$. The position of the electron is $r$. $V(r, R_1, R_2)$ summarizes the three potential energy terms (terms (3), (4), and (5) in equation 3.2). Thus, the Hamiltonian (plugging into equation 3.2) acting on the wave function $\Psi$ is:

$$\hat{H}\psi_{el}\psi_N = \left[-\frac{\hbar^2}{2} \sum_{\alpha=1}^{2} \frac{1}{M_\alpha} \nabla_{R_\alpha}^2 - \frac{\hbar^2}{2m_e} \nabla_r^2 + V(r, R_1, R_2)\right] \psi_{el}\psi_N,$$

(A.1)
which can be expanded:
\[
\hat{H}\psi_{el}\psi_N = -\frac{\hbar^2}{2} \sum_{\alpha=1}^{2} \frac{1}{M_\alpha} \left[ \frac{\partial^2 \psi_N}{\partial R^2_\alpha} \psi_{el} + 2 \frac{\partial \psi_{el}}{\partial R_\alpha} \frac{\partial \psi_N}{\partial R_\alpha} + \frac{\partial^2 \psi_{el}}{\partial R^2_\alpha} \psi_N \right] - \frac{\hbar^2}{2m_e} \frac{\partial^2 \psi_{el}}{\partial r^2} \psi_N + V(r, R_1, R_2) \psi_{el}\psi_N
\]  
(A.2)

Since $M_\alpha \gg m_e$ and $\frac{\partial \psi_N}{\partial R_\alpha} \gg \frac{\partial \psi_{el}}{\partial R_\alpha}$, the terms $\frac{\partial \psi_{el}}{\partial R_\alpha} \frac{\partial \psi_N}{\partial R_\alpha}$ and $\frac{\partial^2 \psi_{el}}{\partial R^2_\alpha} \psi_N$ are approximately zero. Thus, equation A.2 reduces to:
\[
\hat{H}\psi_{el}\psi_N = -\frac{\hbar^2}{2} \sum_{\alpha=1}^{2} \frac{1}{M_\alpha} \frac{\partial^2 \psi_N}{\partial R^2_\alpha} \psi_{el} + \left[ -\frac{\hbar^2}{2m_e} \frac{\partial^2 \psi_{el}}{\partial r^2} + V(r, R_1, R_2) \psi_{el} \right] \psi_N.
\]  
(A.3)

The bracketed term is the electronic Hamiltonian (compare with equation 3.3). Recall that solving the electronic Schrödinger Equation yields the potential energy function, $U(r; R)$, multiplied by the electronic wave function. Replacing the bracketed term in equation A.3 with the potential energy curve, $U(r; R)$, simplifies equation A.2 to
\[
\hat{H}\psi_{el}\psi_N = \left[ -\frac{\hbar^2}{2} \sum_{\alpha=1}^{2} \frac{1}{M_\alpha} \frac{\partial^2 \psi_N}{\partial R^2_\alpha} + U(r; R) \psi_N \right] \psi_{el}.
\]  
(A.4)

The term in brackets is the nuclear Hamiltonian, in agreement with equation 3.5 (Shyur 2011).

\[1\] The nuclei hardly move relative to the electrons, therefore their wave functions are highly localized. Thus, the slopes of their wave functions change far more quickly than those of the electronic wave functions.
Appendix B

Additional Information for the Temperature Controller

B.1 Parts List

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Part</th>
<th>Company</th>
<th>DigiKey Part Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100k Ω thermistor</td>
<td>Honeywell Sensing and Controlling</td>
<td>480 – 3135 – ND</td>
</tr>
<tr>
<td>1</td>
<td>470 Ω resistor</td>
<td>Panasonic Electronic Components</td>
<td>P470FCT – ND</td>
</tr>
<tr>
<td>1</td>
<td>1k Ω resistor</td>
<td>Panasonic Electronic Components</td>
<td>P1.0KECT – ND</td>
</tr>
<tr>
<td>2</td>
<td>820 Ω resistor</td>
<td>Panasonic Electronic Components</td>
<td>P820ECT – ND</td>
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<tr>
<td>1</td>
<td>330 Ω resistor</td>
<td>Panasonic Electronic Components</td>
<td>P330ECT – ND</td>
</tr>
<tr>
<td>2</td>
<td>10k Ω resistor</td>
<td>Panasonic Electronic Components</td>
<td>P10KECT – ND</td>
</tr>
<tr>
<td>2</td>
<td>0.1 µF capacitor</td>
<td>TDK Corporation</td>
<td>445 – 1377 – 1 – ND</td>
</tr>
<tr>
<td>3</td>
<td>10 µF capacitor</td>
<td>TDK Corporation</td>
<td>445 – 1388 – 1 – ND</td>
</tr>
<tr>
<td>1</td>
<td>Bicolour LED</td>
<td>Lite-On Inc</td>
<td>160 – 1058 – ND</td>
</tr>
<tr>
<td>Quantity</td>
<td>Description</td>
<td>Manufacturer</td>
<td>Part Number</td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------------------------------</td>
<td>-------------------------------</td>
<td>-------------</td>
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<tr>
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<td>SparkFun</td>
<td>PRT - 00139(SparkFun)</td>
</tr>
<tr>
<td>1</td>
<td>Voltage regulator, 3.3 V</td>
<td>Texas Instruments</td>
<td>LP2950CDT - ND</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.3/NOPB - ND</td>
</tr>
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<td>LogoChip</td>
<td>Microchip Technology</td>
<td>PIC24FJ32GA002 - ND</td>
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<tr>
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<td>SparkFun</td>
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<td>1</td>
<td>Button</td>
<td>Omron Electronics</td>
<td>SW400 - ND</td>
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<tr>
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<td>USB UART</td>
<td>SparkFun</td>
<td>COM - 00650(SparkFun)</td>
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<td>10kΩ potentiometer</td>
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<td>IRF510PBF - ND</td>
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<tr>
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<td>Slide switch</td>
<td>E-Switch</td>
<td>EG1903 - ND</td>
</tr>
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<td>Dual binding posts for banana plugs</td>
<td>Pamona Electronics</td>
<td>501 - 1316 - ND</td>
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<tr>
<td>1</td>
<td>Double AA battery holder</td>
<td>Keystone Electronics</td>
<td>2465K - ND</td>
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</table>

*Table B.1: Temperature Control Unit Parts List*
Figure B.1: Circuit schematic, generated in EAGLE
B.3 Board Diagram

Figure B.2: Image of printed circuit board, generated in EAGLE
B.4 PicoBlocks Temperature Control Program Code

Figure B.3: The text code environment can be used to write blocks.
Figure B.4: The block code serves as the structure. The LogoChip gathers information from sensors 1-4 and makes decisions according to this tree.
Appendix C

Temperature Conversion Tools

C.1 Plot: Temperature (°C) as a function of PicoBlocks Sensor Number

*Figure C.1: Temperature (°C) as a function of PicoBlocks Sensor Number*
C.2 Python Temperature Converter: TempConv.py

# -*- coding: utf-8 -*-

#Hannah Herde
#PHYS 360 - Thesis 1 - Stark
#October 2013

#Temperature Controller: Temperature Converter
from math import exp, expm1, log
print "Side_Arm_Temperature_Converter"

A = .1616;
beta = 3974;
R1 = 470; #Resistance (ohms) of resistor in series
#with thermistor in voltage divider
Vin = 3.3; #Logochip voltage is controlled to 3.3 V

#Input Sensor 1 (Temperature), Sensor 2 (Setpoint)
N = input ('Thermistor_Number='); #Picoblocks numeric over thermistor/
#sensor 1/Temperature (V)

#Calculate Current Temperature (C) and setpoint
CurrentTemp = (beta/(log((R1*N)/(A*(1000-N)))))-273
print 'Current_Temperature C =',
print CurrentTemp
Appendix D

January 2014 Spectra

For all plots, the absorption spectrum is shown in black. The smoothed background spectrum is red.

Figure 4.1 containing the 130°C spectra can be found in section 4.1.
Figure D.1: Spectra: 120°C side-arm temperature, 550°C absorption cell temperature
Figure D.2: Spectra: 140°C side-arm temperature, 550°C absorption cell temperature
Figure D.3: Spectra: 155°C side-arm temperature, 550°C absorption cell temperature
Figure D.4: Spectra: 175°C side-arm temperature, 550°C absorption cell temperature
Figure D.5: Spectra: 195°C side-arm temperature, 550°C absorption cell temperature
Figure D.6: Spectra: 175°C side-arm temperature, 550°C absorption cell temperature
Figure D.7: Spectra: 195°C side-arm temperature, 550°C absorption cell temperature
Figure D.8: Spectra: 215°C side-arm temperature, 550°C absorption cell temperature
Appendix E

Optical Depth Calculator: Tau.py

```python
import numpy as np
import copy, sys, commands, os, tempfile, datetime, re
from scipy import optimize, signal, interpolate, constants
import warnings, shutil
from math import exp, expm1, log
from numpy import *
from numpy import loadtxt
import time

print "Calculate Optical Depth"

#Select blank and absorption files. These files
#must be in the
#"current directory" in terminal
blank = input('Blank is ');
absorption = input('Absorption is ');

print blank
print absorption

#Read the blank file & create an array of I0
blank_file = open(blank, "r")
blines = loadtxt(blank, dtype = float, comments='#', unpack=False)
blank_file.close()
b = array(blines, dtype=float)
by=b[:,1]
Io=abs(by)
```
print "Io loaded, length is"
len(Io)

#Read the absorption file & create an array of I and wavenumber
absorption_file = open(absorption, "r")
lines = loadtxt(absorption, dtype=float, comments='#', unpack=False)
absorption_file.close()
a = array(lines, dtype=float)
wavenumber = a[:, 0]
ay = a[:, 1]
ay = abs(ay) #I
print "I loaded, length is"
len(ay)

print "Create linear scaling function for Io"
lwv = input('low wavenumber = ');
hwv = input('high wavenumber = ');
lmult = input('Multiplier for low wavenumber = ');
hmult = input('Multiplier for high wavenumber = ');
xo = wavenumber[1];
slope = (hmult - lmult) / (hwv - lwv);
print "slope = "
slope
print intercept = input('Multiplier at starting Wavenumber = ');
n_steps = len(wavenumber);
factor = zeros(n_steps, dtype=float)
for i in np.arange(0, n_steps):
    factor[i] = slope * (wavenumber[i] - xo) + intercept;
    Io[i] = factor[i] * Io[i];

#Write new Io file
f = open('Io.txt', 'w')
for i in np.arange(n_steps):
    f.write('{0:f}\n'.format(wavenumber[i], Io[i]))
f.close()
print "New Io file written"

#Calculate the optical depth
print "Calculating optical depth..."
tauy = zeros(n_steps, dtype=float)
for i in np.arange(0, n_steps):
    tauy[i] = math.log(Io[i] / ay[i])
    #print tauy[i]
    #time.sleep(1)
print "Blank length is"
len(Io)
print "Optical depth file length is"
print len(tauy)

# Write wavenumber and calculated optical depth
# as two-column data
f = open('opticaldepth.txt', 'w')
for i in np.arange(n_steps):
    f.write('{0:f}\n'.format(wavenumber[i], tauy[i]))
f.close()
print "Optical Depth file written"