Photodetachment Spectroscopy of the Negative Sulfur Ion at the $^{2}\text{P}_{1/2}\rightarrow^{3}\text{P}_{2}$ Threshold in an External Magnetic Field

by

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A thesis submitted in partial satisfaction of the requirements for the Bachelor of Science with Honors in Physics at Davidson College

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Abstract

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Photodetachment from the negative sulfur ion in a magnetic field is a well-studied phenomenon at the $^2P_{3/2} \rightarrow ^3P_2$ transition, known as the electron affinity. It is modeled using the Blumberg, Itano, Larson (BIL) Theory. The goal of this work is to apply the BIL theory’s prediction to the less studied $^2P_{1/2} \rightarrow ^3P_2$ transition. A Penning ion trap was used to trap the ions and photodetachment was achieved using a continuous wave tunable dye laser. For the first time, structure in the detachment cross-section due to the magnetic field was observed at this transition. Structure was numerically observed that was consistent with individual Zeeman transitions for the first time at any transition using a 1.0-T magnetic field.
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Chapter 1: Introduction

This work investigates the transition between the $^2P_{1/2} \rightarrow ^3P_2$ states of the negative sulfur ion through photodetachment spectroscopy. This is accomplished by illuminating a cloud of sulfur ions in a magnetic field with photons from a tunable continuous-wave laser. The transition is probed by monitoring the proportion of ions which survive at each light frequency. Much of the previous work on sulfur using this technique has focused on the electron affinity of sulfur, the $^2P_{3/2} \rightarrow ^3P_2$ transition.

This experiment is important for a variety of reasons. The detachment process in a B field is modeled using what is known as the Blumberg Itano Larson (BIL) Theory [4-6]. This theory was developed to model behavior of the system near the electron affinity. In theory the behavior at the $^2P_{1/2} \rightarrow ^3P_2$ threshold should be no different, but until the work undertaken for this thesis it had never been studied in depth. Also, the frequencies at which these transitions occur can be used as spectroscopic benchmarks. For example, the spin-orbit splitting can be found from the difference in the $^2P_{1/2} \rightarrow ^3P_2$ and $^2P_{3/2} \rightarrow ^3P_2$ threshold energies. Furthermore, photodetachment in a magnetic field has applications to other areas of physics such as atmospheric and plasma physics as well as photoionization studies [6, 20].

Photodetachment from a negative ion only occurs when photons with energy above a certain threshold are absorbed by the ion. In the absence of a magnetic field the freed electron can move off in any direction. Therefore detachment is zero below the threshold
frequency and above the threshold it is a monotonically increasing function of light
frequency, according to the Wigner Law [17]. However, in a magnetic field, the motion
of the electrons is quantized and restricted to certain orbits, known as Landau levels or
cyclotron states. This gives structure to the cross-section so that the relation of
detachment to light frequency above threshold is no longer strictly monotonic. Instead,
the cross-section is a series of peaks, each increasing in height. At frequencies much
greater than the threshold, the difference in height between the peaks goes to zero and the
function appears monotonically increasing [4-6].

This is not a complete picture, however. Due to the magnetic field the energy levels of
the ion and the neutral atom split into Zeeman levels. The $^2P_{1/2}$ state becomes two levels
and the $^3P_2$ state splits into five different levels. The ion becoming a neutral atom is no
longer a single transition but many, though not all are allowed due to conservation of
momentum. The series of peaks described above is actually the sum of the various
Zeeman transitions, which are narrower peaks.

The structure in the cross section is due to the superposition of the allowed transitions.
Without the magnetic field there is only a single possible transition: the ion is in a single
state and moves into a single state neutral atom, while the electron goes from its orbit of
the ion to a free state. In the zero field case the only structure is the initial threshold.

With the magnetic field present, the overall structure is caused by transitions of the
electron from its bound state with the ion to any of an infinite number of quantized
cyclotron states. The fine structure is caused by the ion transitioning from one of two ionic states to one of five different neutral states. Depending on the polarization of the light, there are either four (parallel (\(\pi\)) polarization) or eight (perpendicular (\(\sigma\)) polarization) possible transitions. This means that each large peak due to the electron’s transition contains 4 or 8 narrower peaks.

Measurements of these cross-sections are achieved using ions contained in an ultra high vacuum. The ions are held using a static electric field and a static, external magnetic field in a Penning ion trap. By using a changing electric field, the relative number of ions in the trap may be measured.

The results of this work show evidence of magnetic field structure found to be numerically consistent with individual Zeeman transitions. This is the first time that magnetic field structure has been found at the \(^2P_{1/2} \rightarrow ^3P_{2}\) threshold. This data represent the first time at any threshold that evidence for individual Zeeman transitions has been observed using this method with a field strength of 1.0 T. Also, this work yields an independent measurement of the field-free \(^2P_{1/2} \rightarrow ^3P_{2}\) threshold energy.
Chapter 2: Theory

The study of negative ions has interesting applications in many fields of physics. Photodetachment from negative ions in an external magnetic field contributes to the study of atmospheric and plasma physics [7, 14] and covalent bonds [20]. The theory behind this photodetachment has similarities to photoionization [14] and transitions between the valance and conduction band cyclotron states in semi-conductors [6]. This chapter provides the theoretical background for this experiment: first a general overview of negative ion physics and then a detailed explanation of the theory of photodetachment from negative ions in an external magnetic field.

**NEGATIVE IONS**

Negative ions, due to the short range of the interaction between the atom and the excess electron, have only a finite number of bound states [16]. The negative sulfur ion and other isoelectronic species, for example, only have two bound states: $^2P_{3/2}$ and $^2P_{1/2}$. Sulfur is a convenient choice of ion to investigate for several reasons. One can create the negative sulfur ion through a fairly simple reaction using carbonyl sulfide (OCS), an available and relatively non-toxic gas. Using an electron source, the following reaction produces the negative sulfur ion: $e^- + \text{OCS} \rightarrow S^- + \text{CO}$. The sulfur ion can be easily trapped in significant quantities using a Penning ion trap. Both bound states of the sulfur ion are detached at photon energies that are easily generated with Rhodamine 6G and Kiton Red laser dyes. Lastly, sulfur has been used in many of the previous experiments.
that investigated photodetachment from negative ions in a magnetic field [4-6, 12-14, 19, 20].

The Zeeman effect causes the splitting of a single energy level into several energy levels in the presence of a magnetic field. A charged particle has a magnetic moment due to its motion. In the presence of a magnetic field, the total angular momentum precesses around the field axis. But, again due to space quantization, the total angular momentum vector, J, can only be oriented in certain ways with respect to the field axis. The J vector is oriented such that its projection onto the field axis is equal to Mj, which ranges from –J to J in integer steps. With an external magnetic field then, there are 2J+1 Zeeman levels. For states that are not singlet, the anomalous Zeeman effect applies. In this case the energies are weighted by the Landé g factor, a term depending on the J value and L, the angular momentum of the atom. Due to this, the levels are not evenly spaced. Since the energies depend on J, it is clear that both the magnetic moment due to the orbital angular momentum and due to spin cause this effect [11].

**SULFUR**

The states of sulfur which are of interest to this work are the $^2P_{1/2}$ state of the negative ion and the $^3P_2$ state of the neutral atom. The $^2P_{1/2}$ state is the highest energy bound state of the ion; it is part of an inverted doublet with the $^2P_{3/2}$ state. In fact, there are only two bound states in the negative sulfur ion [5]. The ground state of the neutral atom, the $^3P_2$ state, is part of an inverted triplet. In the presence of an external magnetic field, B, the
ionic level $^2P_{1/2}$ splits into 2 Zeeman levels and the ground state of the atom splits into 5 levels, as seen in Figure 2.1.

![Energy Level Diagram](image)

**Figure 2.1:** An energy level diagram for the sulfur ion and the neutral atom. The electron affinity is given in nanometers and the fine structure constant is given in wavenumbers.

**BIL THEORY**

The theory for photodetachment in a magnetic field was developed in 1978 by William Blumberg, Wayne Itano and Dan Larson [4, 5, 6]. This model is known as the BIL theory, after its creators. The aim was to model the detachment profile of negative ions at the threshold of their electron affinity. The electron affinity of an ion is defined as the energy of the transition between the lowest lying bound state of the ion to the ground state of the neutral atom. In the case of sulfur this is the transition between the $^2P_{3/2}$ state
of the ion and the $^3P_2$ state of the neutral atom and it has a value of \(16752.9760(42)\, \text{cm}^{-1}\) in the field free case [1].

In the field free case the near-threshold behavior follows the Wigner Law [17] prediction. The cross section for photodetachment is proportional to \(k\), which is “the relative momentum of the electron and the residual atom in the center of mass frame of reference” [4]. The cross section, \(\sigma\), in more concrete terms, is proportional to the difference between the frequency of the light (\(\nu\)) and the threshold frequency (\(\nu_o\)) to the \(\frac{1}{2}\) power: \[\sigma_{i\rightarrow f} \propto \nu(\nu - \nu_o)^{\frac{1}{2}}.\] This means that the energy of the electron is \(h\nu - h\nu_o\) and it is free to move off in any direction.

When photodetachment occurs in an external magnetic field, the field drastically changes the near-threshold behavior of the cross section. The detached electron is now confined to certain cyclotron states, known as Landau levels. Instead of there being a single threshold at each fine structure transition there is now a periodic structure caused by transitions into the various Landau levels. These thresholds are given by \(h\nu = h\nu_o + (n + \frac{1}{2})h\omega_H\), where \(n\) is the principal quantum number of the Landau level and \(\omega_H\) is the cyclotron frequency \((\omega_H = \frac{eB}{m})\). Physically, the electron wave function is confined to a volume which is small compared to the cyclotron radius as it travels outward from the atomic core with an equal probability in every direction. The structure present in the cross section is due to the electron constructively interfering with itself as it returns to the atomic core. This return to the core occurs once each cyclotron orbit. This interference only occurs in a
region very small compared to the volume defined by the cyclotron radius. This region is approximately within a sphere with a radius equal to the Bohr radius and centered on the neutral core. As this is happening the neutral atom moves away while the electron orbits a stationary point [6].

The BIL theory’s prediction is a sum of the effects of several phenomena. There is a cross section for each Landau level proportional to the density of states, which go as \( \frac{1}{k} \). These cross sections are summed up and coupled with the Zeeman transitions weighted by their strengths and modified by the broadening caused by the Doppler Effect and the motional Stark Effect.

The BIL theory is based on several simplifying assumptions. The first is that of the three quantized motions, axial, cyclotron, and magnetron, only the cyclotron motion is taken into account because only it can be resolved experimentally. Second, electric dipole transitions are modeled using first order time-dependant perturbation theory. Third, the theory’s calculation of the dependence of cross section on photon energy is confined to a small range (approximately 4 wavenumbers) above the threshold. This ensures that the wavelength of the electron is large compared to the range of the force between the electron and the atom. This condition ensures that the final state only involves the wavefunction of the electron and the neutral atom can be neglected [4]. Another assumption is that the strength of the magnetic field is low enough that the electron is confined to a space much larger than the ion. The last assumption on which the original theory was modeled is that final state interactions are insignificant [6]. As dealt with
above, this assumption is incorrect, but can still be ignored since it is below the experimental resolution. The theory also neglected a possible effect on the motion of an electron perpendicular to the magnetic field. This would be an effect similar to the cause of quantum defects in multi-electron atoms. The electron is under the influence of the magnetic field for the majority of its motion, but then scatters off the atomic core. This results in a phase shift in the electron wavefunction and a shift in the energy levels [7]. An experiment found evidence for this effect, but not as large as predicted so it does not affect the cross section [14].

There are two methods that can be used to generate the BIL theory result. The first method expresses the wave functions using the nucleus of the atom as the origin. This method requires another assumption, initially. It is assumed that the Hamiltonian is separable, and later the cross terms due to the motion of the ions are added in. This calculation uses first order time-independent perturbation theory in the form of the golden rule. One might recall that Fermi’s Golden Rule states “that the transition rate is proportional to the square of the matrix element of the perturbing potential and to the strength of the perturbation at the transition frequency” [9]. The perturbation used in this case is $V \cos[\omega t] = -\vec{e} \cdot \vec{P} \cos[\omega t]$ where $V$ is the potential, $\vec{e}$ is the electric field vector, $\omega$ is the photon frequency, and $\vec{P}$ is the electric-dipole moment operator. The transition rate is $\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f \vert V \vert i \rangle \right|^2 \rho(E_f)$ where $\langle f \vert$ is the final state of energy $E_f$, $\vert i \rangle$ is the initial state of energy $E_i$, and $\rho(E_f)$ is the density of final states. The energy of the initial state is related to the energy of the final state by $E_f = E_i + \hbar \omega$. The cross section, defined
as the transition rate per unit flux of photons, is given by \( \sigma_{i\rightarrow f} = \frac{8\pi\hbar\omega}{e^2c^2} \Gamma_{i\rightarrow f} \). This is proportional to the density of final states, which is proportional to \( k \), or \((\nu - \nu_o)^2 \) . So this cross section reduces to the prediction of the Wigner law for detachment into an s state without final state interactions. In a sulfur-like negative ion, with a bound p state electron, the freed electron can enter into either a continuum s or d state. However, a d state would have a very long orbit and not overlap as much with the core and therefore can be ignored [14].

Since final state interactions are ignored, once detached, the electron is essentially a free particle in a homogenous magnetic field. In our experiment, the field is over a volume much larger than the volume of the trap so the field is homogenous over the neighborhood of the interactions. Using the symmetric gauge \( \vec{\mathbf{A}} = \frac{1}{2} \vec{\mathbf{B}} \times \vec{\mathbf{r}} \), so that \( m \) is still a valid quantum number, the eigenfunctions can be written in cylindrical coordinates as \( \Psi = (2\pi)^{-\frac{1}{2}} R_{nm}(\rho)e^{im\phi}e^{ik_zz}/\hbar \). This gives energies \( E = \hbar\omega(n + \frac{1}{2}|m| + \frac{1}{2}m + \frac{1}{2}) + \frac{k_z^2}{2M} \).

The mass of the electron is \( M \), \( k_z \) is the momentum in the z direction, \( n \) is the cyclotron quantum number, \( m \) is the azimuthal quantum number, and \( \omega \) is the cyclotron frequency \( (\omega_c = \frac{eB}{M}) \). Since the electron is detached into an s state, the value of \( m \) is 0 [6].

There is, as mentioned above, an alternate derivation of this result. We start by defining two new quantum numbers \( n_+ \) and \( n_- \) by \( m = n_+ - n_- \) and \( n = n_+ \) for \( m \leq 0 \) and \( n = n_- \) for \( m \geq 0 \).
The quantum numbers $n_+$ and $n_-$ have a classical physical interpretation: $(2n_+)^{1/2} a_H$ is the cyclotron radius and $(2n_-)^{1/2} a_H$ is the distance from the center of the orbit to the z axis.

The energy is, ignoring any motion in the z direction, $E = \hbar \omega \ast (n_+ + 1/2)$. For radii smaller than the zero point cyclotron radius, $R_{nm}(\rho) \approx \frac{1}{a_H m!} \left( \frac{(n + |m|)!}{n!} \right)^{1/2} \left( \frac{\rho}{\frac{1}{2} \frac{1}{2} a_H} \right)^{|m|}$. As with the other formulation, $m=0$ since only s states will return to the core. Also, due to the fact that the parity must change in an electric-dipole transition, the final state must have an even parity. Therefore the final state is given by $\Psi_n = (2\pi)^{-1/2} R_{n0}(\rho) \cos\left(\frac{k_z z}{\hbar}\right)$ with an energy of $E = \hbar \omega (n + \frac{1}{2}) + \frac{k_z^2}{2M}$. This matches what the other method gives for the energies when $m=0$. In this state, $n_+ = n_-$ and can be interpreted as a superposition of cyclotron states which intersect the origin, which in this coordinate system is the neutral atom [6].

The cross section depends on a density of states function which is caused by the one dimensional continuum in the z direction and is proportional to $\frac{1}{k_z}$. The cross section, now including Zeeman states, is given by $\sigma(\nu) = \sum_{n=0}^{n_{\text{max}}} \sigma(\nu) = \frac{D \nu^{n_{\text{max}}}}{a_H^2} \sum_{n=0}^{n_{\text{max}}} (\nu - \nu_n)^{-1/2}$ where $n_{\text{max}}$ is the largest $n$ for which $\nu - \nu_n$ is positive. $D$ is a constant which does not depend on $\nu$ or H. At small fields with a low experimental resolution, this sum can be approximated by
an integral: 
\[
\sigma(v) = \frac{2\pi MDv}{h} \int_{v_o}^{v} (v - v')^{-1/2} dv',
\]
which yields 
\[
\sigma(v) = \frac{2\pi MDv}{h} (v - v_o)^{1/2},
\]
which is the Wigner Law [6].

The two derivations above neglect the motion of the ion in the calculation of the cross section. There are two major motional effects that the BIL theory takes into account: 1. the Doppler Effect and 2. the motional Stark Effect. Each of these effects causes a broadening of about 1 GHz [6].

The Doppler Effect shifts the frequency of the light in the frame of the ion by
\[
\nu \rightarrow \nu - \nu \kappa \frac{v}{c},
\]
where \( \nu \) is the velocity of the ion, \( \kappa \) is the unit vector in the direction that the light propagates, and \( \nu \) is the frequency of the light in the lab frame. In our experiments, \( \kappa \) is perpendicular to the direction of the field. Assuming the most probable velocity \( 7 \times 10^4 \) cm/sec, this gives a frequency shift of approximately 1.2GHz to the photons [6].

The Stark effect is the well-known splitting of spectral lines caused by the presence of an external electric field. It is the analog of the Zeeman effect in an electric field. The field causes the angular momentum vector \( J \) to precess around the direction of the electric field. This causes a quantization of \( M_j \). Because the ion ensemble in the trap has thermal energy the ions are in motion. They are also in a magnetic field, so the ions feel an electric field in the coordinate system that moves with the ions. The ions feel an electric field which is described as
\[
\vec{E} = \vec{v} \times \frac{\vec{B}}{c}
\]
where \( \vec{v} \) is the velocity of the ion and \( \vec{B} \) is the
magnetic field. This field is perpendicular to the magnetic field and pushes the electron away from the core. This causes the experimental resolution of the magnetic field structure to become diminished. When this field is on the order of 10V/cm, the magnetic field structure is entirely unable to be resolved [20]. This motional field depends on the ratio between the kinetic energy of the electron when detached, $\frac{1}{2}Mv_x^2$, and the cyclotron energy, $\hbar\omega$. The existence of this field makes it necessary to use the eigenfunctions for an electron in crossed E and B fields [6].

The Schrödinger Equation for this system is a simple harmonic oscillator and the energies can be written as $E(n,k_z,\nu_z,k_x) = (n + \frac{1}{2})\hbar\omega_H + \frac{k_z^2}{2M} - M\nu_H\nu_y - \frac{1}{2}Mv_x^2$ where $y_o = \frac{ck_x}{eH}$. For ions at a velocity of $v_x$, the cross section can be calculated with the following integral: $\sigma_{\nu\rightarrow\nu'} = \frac{2\pi|S|^2}{\hbar^2c} \left( \frac{2\omega_Ha_H}{\nu_x} \right)^{\frac{1}{2}} \int_0^\infty t^{\frac{1}{2}} |\Psi_n(z + t)|^2 \, dt$, where $z = \frac{[E_o + (n + \frac{1}{2})\hbar\omega_H + \frac{1}{2}Mv_x^2 - \hbar\nu]}{M\omega_Ha_H\nu_x}$ and $t = \frac{k_z^2}{2M^2\omega_Ha_H\nu_x}$. Also, $S$ is defined as $\int \Psi^* (\vec{r})\hat{\epsilon} \cdot \vec{P} d^3r$ ($\hat{\epsilon}$ is the unit polarization vector), $\Psi_n(q) = \frac{1}{\pi^{\frac{3}{2}} a_H^2 (2^n n!)} e^{-\frac{q^2}{2}} H_n(q)$, $n=0,1,2,3\ldots$, $q = \frac{(y - y_o - \nu_y)}{a_H}$, and $H_n$ is the Hermite Polynomial of order $n$ [6].
We can find a velocity-averaged cross section for light propagating perpendicular to the z axis. 

\[
\frac{1}{\pi v_o^2} \int_0^\infty \sin^2 \theta d\theta \exp \left( \frac{-v^2}{v_o^2} \right) \sigma_{j\rightarrow n}(v, \nu_x) \quad \text{where} \quad v_o = \sqrt{\frac{2k_B T}{M_i}},
\]

\[\nu = \frac{\nu}{c} (1 - \frac{v}{c} \cos[\theta]) \quad \text{and} \quad \nu_x = \nu\]

where \(M_i\) is the mass of the ion, \(T\) is the temperature and \(k_B\) is Boltzmann’s constant [6].

It turns out that the different Zeeman transitions are not all equally probable. The different cross sections must be weighted according to the probabilities of their transitions. Given an initial state \(|i> = |p^5s^2p^*J^*M>\) (\(p^5\) and \(p^*\) are the states of the electrons and ion respectively, \(J\) is the total angular momentum, and \(M\) is its \(z\) component), assuming LS coupling is valid for the \(S^+\) ion and the \(S\) atom and a final state of the electron \(|f> = |p^43p^*m^j;i^2S)*1/2*m_c>\) the relative transitions strengths are the absolute square of the matrix element of the electric dipole operator \(P_q^{(i)}\) between initial and final state. In the electric dipole operator \(q=0\) for pi polarization, \(\pm 1\) for circularly polarized light and the components are summed over \(\pm 1\) for sigma polarization. Inserting an intermediate state \(|(L'S')^J'M'>\) and projecting it on the final state gives

\[
\langle f | P_q^{(i)} | i > = \sum \langle (^iP)jm;i^2S) | (J^1/2)M'> \langle (J^1/2)J'M'| (L'S')J'M'> \langle (L'S')J'M'| P_q^{(i)} | p^5(^2P)JM >
\]

Then by using the Wigner-Eckart theorem, which allows the transfer of operators between bases using the Clebsch-Gordan coefficients and using the Wigner 3-j and 6-j
symbols to represent the angular momentum coupling coefficients, we find the final form
\[ < f | P_q^{(i)} | i > = (-1)^{i+j-j'}[2(2j + 1)(2J + 1)]^{1/2} < f \parallel P^{(i)} \parallel i > \]
\[ \times \sum_{J'M'}(2J'+1) \left( \begin{array}{ccc} J' & 1 & J \\ -M' & q & M \\ m & m_e & -M' \end{array} \right) \left( \begin{array}{ccc} 1 & 1 \ 1/2 & J' \ 1/2 & J' \end{array} \right) \left( \begin{array}{ccc} 1 & 1 \ 1/2 & J' \ 1/2 & J' \end{array} \right) \]
These weighting coefficients are essential to accurately predicting the structure of the cross section based on the polarization and light frequency [6].

The ultimate equation which predicts the structure of the cross section is
\[ \sigma_i(v_{lab}) \propto \sum_k < \sigma_{i\rightarrow k}(v_{lab}) >_{av} | < f | P_q^{(i)} | i > |^2 \] [6]. The cross section at a given frequency is determined by a combination of the cross sections of the individual Zeeman transitions, weighted by the likelihood of that transition.
Chapter 3: Experimental Setup & Procedures

We determined the relative cross section for detachment from $^{32}$S$^-$ in the presence of a 1 Tesla magnetic field by observing the depletion of an ion cloud stored in a Penning ion trap when the ions were illuminated by a ring dye laser [15]. This technique has been used in many previous experiments that studied photodetachment from negative ions [4-6, 12-15, 18-20].

The sulfur ions were created in the Penning trap by bombarding carbonyl sulfide gas with electrons produced by a thoriated tungsten filament. This technique is known as dissociative attachment. The goal of this process is to cause the following reaction:

$$\text{OCS} + e^- \rightarrow ^{32}\text{S}^- + \text{CO}.$$  

This process occurs in an ultra high vacuum, at a pressure of approximately $3 \times 10^{-8}$ Torr, which is about $10^{10}$ lower than atmospheric pressure. A variable leak valve controls the flow of gas into the trap. A typical ensemble used in an experiment has approximately $10^4$ ions [15]. The experiment itself does not measure an absolute number of ions, however; instead the relative number of ions is measured and compared before and after laser illumination.

**APPARATUS**

A Penning ion trap consists of a single ring electrode and two endcap electrodes. The surfaces of the electrodes, which are hyperboloids of revolution, are given by the following equations:

$$r^2 - 2z^2 = \pm 2z_0^2 \quad (+\text{ring}, -\text{endcaps})$$
\[ r_0^2 = 2z_0^2 \]

The value \( z_0 \) is the distance from the center of the trap to the endcaps along the central axis, which, for this trap, is 2.54mm. The radius of the ring electrode, the distance from the center to the inner surface, \( r_0 \), is 3.5814mm, see Figure 3.1 [4]. Penning traps use a static DC potential on the end cap electrodes to create a harmonic well to trap the ions along the \( z \) axis. A static axial magnetic field is applied to trap the ions on the \( x-y \) plane [8].

\[ \text{Figure 3.1: A schematic of the ion trap [18].} \]
Applying a radio frequency (RF) potential at a specific frequency to the endcaps causes
the ion cloud to undergo resonant axial motion. The ring electrode is connected to
ground, so the motion of the ions induces a current, called the image current, on the ring
electrode. Because the ions move past the ring electrode twice for each oscillation, the
current flowing between the ring electrode and ground is at twice the driving frequency.
If the trap is electronically balanced correctly using a variable capacitor, the ring
electrode picks up virtually none of the driving voltage from the endcaps, meaning the
current measured is due entirely to the ion cloud’s motion [15].

The radio frequency applied to the endcaps selects the ion species to be trapped. The
resonant driving frequency is determined by \( \nu_z = \frac{\omega_z}{2\pi} \) where \( \omega_z \) satisfies
\( \omega_z^2 = -\frac{e\phi_B}{mz_o^2} \)
and \( \phi_B \) is the voltage between electrodes, \( m \) is the mass of the species to be trapped and \( z_o \)
is 2.54mm [4]. The potential causes only the ions of mass \( m \) to oscillate in the trap. This
gives better than 1 amu mass resolution so that we can be sure that we are only measuring
the amount of \( S^- \) in the trap and not any of the background gases.

The image current is then detected using a heterodyne receiver, see Figure 3.2. The
receiver consisted of a tuned parallel resonant LC circuit with the inductor kept at 77K by
a bath of liquid nitrogen. This converts the image current into a voltage. The circuit was
cooled to increase the Q value of the circuit and to limit thermal noise. The detector was
capacitively linked to a field effect transistor (FET) voltage follower, which served as a
buffer between the receiver and the rest of the detector electronics. [4]
Figure 3.2: A schematic of the trap electronics [18].

The FET is followed by a cascode amplifier with a maximum gain of 1600. The final component of the heterodyne detection scheme is a Perkin Elmer lock-in amplifier. A lock-in amplifier filters and amplifies a signal at a desired frequency, in this case the frequency of the image current, then converts it to a DC voltage proportional to its amplitude. This DC signal is read by the computer through an analog to digital (ADC) board which is interfaced with a LabVIEW program which controls the entire apparatus.
The laser system used to photodetach the ions was a modified 899-05 Coherent ring dye laser. This is a passively stabilized tunable dye laser system which is computer controlled. The major optics of the laser cavity include a birefringent filter, a set of etalons, a scanning Brewster plate, and a tweeter mirror. The gain medium is Kiton Red dye and the pump laser is a 5W solid state, diode-pumped, frequency-doubled Neodymium Vanadate laser at 532 nm. The pump laser is water cooled using a Cole Parmer Polystat refrigerated recirculator.

The birefringent filter is the most coarse frequency selection mechanism. Using a series of specifically oriented glass plates the filter can select an order of frequencies with a full width at half maximum (FWHM) of 2 THz. Within this peak finer frequency control can be attained using the other optics.

The etalon assembly includes both a thick and thin etalon system which allows for fine frequency selection. The thick etalon is controlled with a piezoelectric crystal and the thin etalon is controlled by a galvanometer. The thin etalon allows for coarse frequency selection between orders of 200 GHz FWHM. The thick etalon allows for fine control of the frequency in orders of 5 GHz FWHM. The combination of these optics allows continuous frequency selection within these orders.

The laser is controlled by a LabVIEW virtual instrument that allows the user to set the voltage applied to the piezoelectric crystals and current through the galvos. As currently
configured, the computer uses 2 DAC boards to output voltages to control both the thick and thin etalons simultaneously. These voltages range between 1.1V and 3.8V for the thick etalon and are amplified by a homemade driver consisting of op-amps to range between 110-380V. The thin etalon uses voltages which range from -2.71V to 1.2V. The VI also monitors the laser wavelength, mode and linewidth, see Figure 3.3.

The wavelength is measured using a Burleigh brand wavemeter. The vacuum wavelength setting is used because the interior of the trap is closer to vacuum than atmosphere. It can measure the wavelength to within .01 wavenumbers and displays it on the user interface. The laser mode and bandwidth are measured using a Fabry-Perot spectrum analyzer with a free spectral range of 8 GHz.
In order to insure that there is a consistent flux of light through the trap on each data run a photodiode located behind the trap and a shutter located in front of the trap are used. The computer opens the shutter, uses feedback from the photodiode to determine an integrated light flux and closes the shutter.

During operation, the ion trap is kept at approximately $3 \times 10^{-8}$ Torr by an ultra high vacuum system. The system is pumped down first by a sorption pump to a rough vacuum and then by an ion pump. The sorption pump can reach pressures of $10^{-2}$ or $10^{-3}$ Torr. The ion pump then takes the system down to the experimental pressure. With the leak valve closed, the system is typically pumped down to a background pressure of approximately $1 \times 10^{-10}$ Torr. The final major feature of the vacuum system is the cross of stainless steel which holds the ion trap. This cross has two view ports, one on each end of the horizontal arm of the cross. These ports allow laser light to be directed into the trap and then to exit to the photodiode. The vertical arm of the cross attaches to the ion pump and the leak valve. The bottom of the cross attaches to an electronics feedthrough, where the driving RF and trapping RF are applied to the trap and the image current enters the detection electronics. The feedthrough also serves as a mount to place the trap into the center of the UHV cross.

The final component of the apparatus is the magnet. The magnet used is a Varian V7700 water cooled electromagnet. It is capable of creating fields of up to ~2 Tesla, but in this experiment we only use a field of 1 T.
EXPERIMENT

An experiment begins by allowing the electronics a warm up time. It is felt that the system gives more consistent results with smaller error if it is allowed to warm up for a period of at least 90 minutes. The electronics that especially need to warm up are the magnet power supply, the water pump, and the detection electronics.

After the warm up period the leak valve is opened to give a pressure of approximately \(3 \times 10^{-8}\) Torr. The system is then run without the laser for about 5 to 10 minutes until a sufficient amount of ions are created. Also, liquid nitrogen (LN\(_2\)) is added to the detection system. The LN\(_2\) supply is replenished anytime there is an extended period of high error on the data, or every few hours. Finally, the photodiode behind the trap is aligned with the laser beam through the trap.

A typical data set consists of data points separated by a tenth of a wavenumber from 16269.80 to 16271.00 wavenumbers. Each data point is made up of roughly 40 cycles and each cycle consists of 5 data runs each. This is the limiting factor on the range of wavenumbers over which data is taken. It takes, on average, 14 to 18 straight hours to take a data set of this size.

Each data run consists of a light run and then a dark run. A light run begins with a background measurement using the detection electronics. Then there is the gas phase in which the ions are created. A negative voltage is applied to the filament to send the electrons into the trap, creating S- from the OCS gas. This phase lasts \(~7\) seconds. The
next step is the initial ion measurement. An RF voltage is applied to the endcaps driving the motion of the ions. This is followed by the optical interaction, or blast, period. The light flux that must be detected by the photodiode is set with a unit-less value on the computer control. Typically at a laser power of approximately 120 mW at these frequencies, measured at the laser, this period should last approximately a second. Then, after the blast period, there is another ion measurement phase. The length of time the program waits between the two ion measurement phases and the time that the shutter is open are independent. Obviously, however, the computer makes sure that the time the shutter is open is finished before measuring the ions again. The difference between the blast time and the time that the trap is illuminated should be as small as possible to avoid trap losses by causes other than photodetachment. A dark run is exactly the same as a light run, but without ever opening the shutter. The time between the “before blast” ion measurement and the “after blast” measurement is kept exactly the same as the time for the immediately previous light run.

A data cycle is the combination of 5 consecutive data runs. The ratios of the after blast ion measurement to the before blast measurement of all five light runs are averaged, and so are the dark run ratios. Then the average light ratio is divided by the average dark ratio to give the “ratio of ratios.” A data point is complete when the error on the weighted average of the ratio of ratios at that frequency is below ~1%. At this point the laser frequency is shifted and another data point is begun.
In this chapter several data runs are compared with theoretical fits. This allows a prediction for the transition threshold to be made and compared to theory. To the best of the author’s knowledge, the data shown here are the first to show magnetic field structure at this transition. More significantly, the data appear to show the first evidence for Zeeman transitions recorded by this method at any transition. Also discussed are the potential errors in the experiment and the theoretical fits.

Several data runs were successfully taken at in a magnetic field of .998 ± .001 Tesla with light polarized parallel to the magnetic field. Light of this polarization is known as pi polarized light. The data sets are shown below with theoretical fits in Figures 4.1 through 4.8.
Figure 4.1: A data set taken with a magnetic field of 1 T and parallel polarization ($\pi$). Notice the first three points have over 100% of ions surviving photodetachment. Also notice the structure of the data, i.e. the fraction surviving is not simply a monotonically decreasing function of light frequency.

The theoretical prediction for the above data set fits the data with a $X^2$ value of 1.06. It predicts a transition threshold of 16269.34 ± 0.002 cm$^{-1}$, which disagrees with the accepted value of 16269.4408(54) cm$^{-1}$ [1]. The point on the theoretical fit at 16270.62 cm$^{-1}$ is likely an anomalous point due to numerical errors in the fitting program. Note that the first three points show evidence of the excess ion problem, showing over 100% of the ions remaining after detachment.
The excess ion problem is the name given to phenomena of the apparent creation of ions during photodetachment. This was noticed in the very first experiments on negative ion photodetachment in a magnetic field [4]. It is thought to be caused by the fact that the reaction which creates negative sulfur ions from OCS is not the only reaction that occurs when OCS is bombarded with electrons. Another possible reaction is to create $S_2^-$ through the reaction $S^-+\text{OCS} \rightarrow S_2^-+\text{CO}$. The threshold for detachment of $S_2^-$ is much lower than either of the $S^-$ thresholds, so it will definitely be photodetached. The following reactions show how the photodetachment of $S_2^-$ can create $S^-$:

$$h\nu + S_2^- \rightarrow e^- + S_2$$
$$e^-+\text{OCS} \rightarrow S^-+\text{CO}$$

If this occurs at a faster rate than detachment, then there potentially will be more $S^-$ than before the blast phase.

All previous photodetachment measurements in a magnetic field at this threshold had found the fraction of ions surviving detachment to be a monotonically decreasing function of light frequency. None of the expected structure has previously been resolved. These data, however, show structure and that structure is reflected in the fit as well. This structure is most likely due to the transitions between the various Zeeman levels.
Figure 4.2: Data set 1 shown with the possible Zeeman thresholds indicated by arrows.

The above Figure 4.2 is marked with arrows where the apparent Zeeman transitions occur in the fit. While the frequencies do not match the theoretical values, the spacing between the transitions matches the theoretical spacings. One feature that gives confidence that these apparent transitions are the actual Zeeman transitions is that the difference between the experimental and theoretical transitions are about -0.10 cm\(^{-1}\), as indicated in Table 4.1. This is the same difference between the predicted and actual field-free transition frequency.

**Table 4.1:**

<table>
<thead>
<tr>
<th>Transition</th>
<th>Experimental Wavenumbers</th>
<th>Spacing</th>
<th>Theoretical Wavenumbers</th>
<th>Spacing</th>
<th>Experimental-Theoretical Wavenumbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>16269.70</td>
<td>.24</td>
<td>16269.83</td>
<td>.23</td>
<td>-0.13</td>
</tr>
<tr>
<td>3</td>
<td>16269.89</td>
<td>.19</td>
<td>16269.99</td>
<td>.16</td>
<td>-0.10</td>
</tr>
<tr>
<td>4</td>
<td>16270.13</td>
<td>.24</td>
<td>16270.22</td>
<td>.23</td>
<td>-0.09</td>
</tr>
</tbody>
</table>
DATA SET 2:

**Figure 4.3:** Data Set 2, taken at 1T using π polarized light. While the data shows structure, the theoretical fit does not.

This data set predicts a transition threshold of 16269.50 ± .714 cm$^{-1}$. The $X^2$ value for this fit is .936. Unfortunately the fit does not reflect the structure apparent in the data. It was believed that this structure may also be individual Zeeman transitions. The poor fit makes finding the possible Zeeman transition thresholds more difficult. For this set, instead of using the model to find the possible thresholds, predictions were made using the data points.
The transitions for the most part match up very well with the theoretical values. The last three transitions are off by hundredths of a wavenumber from the theoretical values. This, however, does not accord with the prediction of the threshold frequency. The fitting program predicts a transition of $16269.50 \pm .714 \text{ cm}^{-1}$, which is about .06 cm$^{-1}$ greater than the theoretical value. The Zeeman levels are not similarly shifted, but the first apparent Zeeman level is at $16269.50 \text{ cm}^{-1}$, the predicted threshold value (see Table 4.2).

One reason that this could be is the prediction of the threshold has a large uncertainty, therefore these Zeeman transitions could be correct.

Table 4.2:

<table>
<thead>
<tr>
<th>Transition</th>
<th>Experimental Wavenumbers</th>
<th>Spacing</th>
<th>Theoretical Wavenumbers</th>
<th>Spacing</th>
<th>Experimental-Theoretical Wavenumbers</th>
</tr>
</thead>
<tbody>
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<td>16269.50</td>
<td>-</td>
<td>16269.60</td>
<td>-</td>
<td>-0.10</td>
</tr>
<tr>
<td>2</td>
<td>16269.81</td>
<td>.31</td>
<td>16269.83</td>
<td>.23</td>
<td>-0.02</td>
</tr>
<tr>
<td>3</td>
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<td>.17</td>
<td>16269.99</td>
<td>.16</td>
<td>-0.01</td>
</tr>
<tr>
<td>4</td>
<td>16270.20</td>
<td>.22</td>
<td>16270.22</td>
<td>.23</td>
<td>-0.02</td>
</tr>
</tbody>
</table>
Figure 4.5: Data Set 3 at 1T and π polarized light. Note the excess ion effect on the first four data points. The fit does not reflect the small amount of structure in the data.

This data set shown in Figure 4.5 has the worst agreement with the theoretical prediction and a $X^2$ value of 3.55. It predicts a transition threshold of $16269.08 \pm .0001$ cm$^{-1}$. Note that this set has very clear evidence of the excess ion problem, with three points above 100% survival. This data run shows far less structure than the others, which may be related to the excess ion problem. No Zeeman transitions are apparent from this data set.
Figure 4.6: Data set 4 taken with a 1T field and $\pi$ polarized light. This set is significant because it covers nearly 3.5 wavenumbers of frequency. This set does not have apparent excess ions. Also, structure can be very clearly seen throughout the set.

The predicted transition threshold for this data set is $16269.33 \pm 0.001 \text{ cm}^{-1}$. The chi-squared value of this fit is 1.26. This set also shows possible Zeeman transitions as shown by the arrows in Figure 4.7.
Figure 4.7: Data set 4 with possible Zeeman transitions indicated by arrows. This set may show up to 8 transitions from the n=0,1, and 2 cyclotron states.

This data set is over a much larger range of frequencies and allows investigation of cyclotron sets of higher orders. Therefore instead of simply seeing four transitions, this set appears to have eight transitions over the first three cyclotron states, see Table 4.3.

Table 4.3:

<table>
<thead>
<tr>
<th>Transition</th>
<th>Experimental Frequency</th>
<th>Spacing</th>
<th>Theoretical Frequency</th>
<th>Spacing</th>
<th>Experimental-Theoretical Wavenumbers</th>
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</tr>
<tr>
<td>2</td>
<td>16269.83</td>
<td>0.19</td>
<td>16269.83</td>
<td>0.23</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
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<td>0.23</td>
<td>16269.99</td>
<td>0.16</td>
<td>0.07</td>
</tr>
<tr>
<td>4</td>
<td>16270.31</td>
<td>0.25</td>
<td>16270.22</td>
<td>0.23</td>
<td>0.09</td>
</tr>
<tr>
<td>5</td>
<td>16270.57</td>
<td>0.26</td>
<td>16270.53</td>
<td>0.31</td>
<td>0.04</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>16270.76</td>
<td>0.23</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>16270.99</td>
<td>-</td>
<td>16270.92</td>
<td>0.16</td>
<td>0.07</td>
</tr>
<tr>
<td>8</td>
<td>16271.27</td>
<td>0.28</td>
<td>16271.15</td>
<td>0.23</td>
<td>0.12</td>
</tr>
<tr>
<td>9</td>
<td>16271.47</td>
<td>0.20</td>
<td>16271.46</td>
<td>0.31</td>
<td>0.01</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-</td>
<td>16271.70</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>-</td>
<td>-</td>
<td>16271.85</td>
<td>0.15</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>-</td>
<td>-</td>
<td>16272.09</td>
<td>0.24</td>
<td>-</td>
</tr>
</tbody>
</table>
Again, the differences between the predicted and theoretical Zeeman transition frequencies do not match the difference between the predicted and theoretical threshold. The locations of the missing transitions are shown on the plot below.

**Figure 4.8:** Data set 4 showing the location of the “missing” transitions.

**ANALYSIS**

The predicted transition for the $^2\text{P}_{1/2}$ to $^3\text{P}_2$ level of the negative sulfur ion is $16269.4408(54)$ cm$^{-1}$ [1]. In the presence of a 1 Tesla magnetic field, the first Zeeman threshold occurs at $16269.60$ cm$^{-1}$. Using all four of the data sets, our predicted threshold is $16269.08 \pm .0001$ cm$^{-1}$. Excluding the 8/30/06 set which is a very poor fit compared to the other three, we find a threshold of $16269.33 \pm .001$ cm$^{-1}$. Clearly, neither of these agrees with the theoretical value.

One possible explanation for the discrepancy is the excess ion problem. The electron affinity of $S_2^-$ is $13,469.45$ wavenumbers [10] so at the frequencies that this experiment
uses the $S_2^-$ population should be thoroughly detached. Therefore the excess ion problem creates excess $S^-$ at a constant rate over the interval of a data run. Since the rate of $S^-$ detachment is not constant over the interval, the excess ion effect is not a mere shift but also a vertical stretching of the curve. In other words, the parts of the detachment curve with low detachment are shifted farther up than areas of high detachment. This might cause the fitting model to report a lower value for the electron affinity, since the slope of the curve will be steeper. Figure 4.9 below shows an exaggerated hypothetical example. Assuming that the fitting program detects the field-free threshold based on the slope of the curve, a steeper curve would cause the program to predict a lower threshold energy. The excess ion curve is the same curve as the no excess ion curve with the data showing no detachment and data showing detachment shifted by different rates. The two vertical lines display how the threshold (the solid line) might be apparently shifted to a lower energy due to the excess ion effect (the dotted line).

**Figure 4.9:** A hypothetical plot showing how the excess ion problem might cause an apparent shift in the threshold (solid line) to a lower value (dotted line).
The disagreement between the measured and previously published transitions is not due to an un-calibrated wavemeter; its calibration was checked with a known light frequency, a HeNe laser. At most the reading is off by 0.02 wavenumbers. It is also unlikely that the data collection system is in error, since it was used to measure the electron affinity of S\(^{-}\) and O\(^{-}\) recently and was in good agreement with other published values. One way to try to ensure that the data collection system was not at fault was to make sure that the heterodyne detector is filled with liquid nitrogen so that it operates at its optimal temperature. This maximizes the sensitivity of the detection system to S\(^{-}\). Hopefully a system more sensitive to S\(^{-}\) will more accurately represent the true sulfur ratios.

There are two possible reasons for the disagreement between the experimental value and the theoretical value. The first reason is the excess ion problem. Depending on how much S\(_2\)\(^{-}\) is created, the rate of its detachment, and the rate at which excess S\(^{-}\) is created the results of the run could be distorted. The excess ion effect has been observed at the \(^2P_{3/2}\)\(\rightarrow\)\(^3P_{2}\) threshold and would be an even larger effect at this transition because there are fewer ions in the \(^2P_{1/2}\) state than in the \(^2P_{3/2}\). Ions in the \(^2P_{1/2}\) state make up only about 20% of the total ensemble. Since there are a small number of ions in the higher energy state, any excess ions created compose a larger proportion of the total ion population. Since the behavior of the process which creates excess S\(^{-}\) is not well known, it is difficult to say how it would affect a data run.

The solution proposed to mitigate the excess ion problem was to use an RF signal to drive S\(_2\)\(^{-}\) out of the trap. In the first iteration this RF signal was applied to the endcaps using a
gated function generator during the blast phase. The application of RF during the blast phase both interfered with the precision of the data and did not prevent the excess ion problem. When applied to the trap during the gas phase it helped to lessen the occurrences of the excess ion problem, but did not totally eliminate it. It is uncertain why this did not eliminate the problem totally.

The second reason that the theoretical fit does not match the structure in the data completely is due to the fitting program. There is not a very large range between the background pre-detachment level and the bottom of the after threshold dip. The other structure in the data is small compared to this dip. Since the curve is fit to the data by minimizing $X^2$ and the data has a small range, $X^2$ may be minimized with a straight line through the data or by ignoring the structure.

**DATA ANALYSIS METHODS**

The data analysis is accomplished by a program which attempts to fit a curve to the data to minimize chi squared. This code is based on a program from Bevington [3] and was created for some of the initial work on the photodetachment of negative ions. The program is actually made up of three programs: VCUR, FUNCTION, and FDERIV [See Appendix C]. The programs find a least squares fit based on various parameters. The fixed parameters are the magnetic field strength, the light polarization, and the transition intensities. The fitted parameters are the baseline detachment ratio, the electron affinity, the coefficient of detachment, the integrated photon flux and the deviation in the thermal Gaussian convolution interval. The formula which the program fits to is Ions
surviving = A + B(e^{-\sigma(2)*F} + e^{-\sigma(3)*F}), where A is the baseline detachment ratio and B is a unitless coefficient of detachment. The integrated photon flux, F, is proportional to, but not the same as the integrated photon flux which is used in the LabVIEW program to control the trap. \( \sigma(2) \) and \( \sigma(3) \) are complicated functions which rely on the Landé g factors, the photon energy, the Bohr magneton and the initial and final quantum numbers. This program is run multiple times manipulating which of the fitted parameters are held constant until \( X^2 \) is approximately 1.
CONCLUSIONS

The experiment on the whole was a success. Data sets were successfully acquired and the theory is fit to the data at the $^2P_{1/2} \rightarrow ^3P_2$ threshold. The theoretical fit allowed a threshold value for this transition to be calculated. Unfortunately there were many technical hurdles that needed to be overcome. However, there are many other experiments which can build from this one.

The major result of this experiment is that magnetic field structure was observed for the $^2P_{1/2} \rightarrow ^3P_2$ threshold. The structure matches the prediction curves fairly well. For example, in data set 1, the spacing between the Zeeman levels match to a few hundredths of a wavenumber. Further, the field-free threshold and the Zeeman transitions suggested by the data are all shifted roughly a tenth of a wavenumber lower than the expected values. Likewise in data set 4, the data show potential Zeeman thresholds which match the theoretical values to within about 0.1 wavenumbers. This suggests that the data show numerical evidence consistent with individual Zeeman thresholds.

This is the first time that any structure has been observed at this threshold for the sulfur ion. It is also the first confirmation of the BIL theory at this threshold. Previous attempts at photodetachment in this regime found “ion depletion to be a monotonically increasing function of light frequency” a range of about 3.7 cm$^{-1}$ above threshold. It was believed that structure was not resolved because the laser linewidth was too large [4]. The use of the ring dye laser, which was not available during the original work by Blumberg, made
concerns about laser linewidth irrelevant. In Blumberg’s work at the relevant frequencies the frequency width of the laser was about 0.7 cm$^{-1}$ which is about three times larger than the spacing of the structure [4]. The linewidth of the ring dye laser is 1000 times smaller. One can say with confidence that the structure observed here is likely due to the magnetic field.

In order to find this structure various technical hurdles were overcome. The excess ion problem plagued most of our early efforts and the efforts of previous physicists. Previous work encountered excess ions even at the $^{2}\text{P}_{3/2} \rightarrow ^{3}\text{P}_{2}$ transition. Due to technical limitations previous physicists were unable to apply their suggested solution of an RF signal during ion formation to drive the $S_{2}^{-}$ out of the trap [4]. The solution, when applied, apparently worked fairly well. While applying the RF signal during ion formation, incidents of over 100% of ions surviving detachment occurred much less frequently. It is not clear if this solved the excess ion problem, but it eliminated the most obvious symptom. This technique can be applied to future work at this and other thresholds.

Another success of the experiment was obtaining a value for the field-free transition energy. This success is partially due to the fact that this experiment resolved real structure that could be fitted using our fitting program [see Appendix C]. The other part of this success is that enough good data runs were collected to get a result. Of the twenty-two data sets collected, only four were actually good enough to fit to. There was a variety of reasons for sets not being useable for fitting, some well understood and some
mysterious. Some sets ran into simple or other understood problems, such as running out of liquid nitrogen for the inductor, or the excess ion problem. Others suffered from inexplicably large error bars which made data taking a lengthy process; too lengthy to get enough points to fit. It is not known what caused this problem. The entire experiment suffered from higher measurement error than previous experiments using this apparatus to measure photodetachment from S\textsuperscript{-} and O\textsuperscript{-}. Adding liquid nitrogen to the detection inductor seemed to help at times. Trying to optimize the trap by adjusting the settings of the program which controlled it and the physical electronics seemed to have some effect as well. Also, changing the pressure was tried. None of these actions solved the problem. The only solution which was a suitable work around was to take lots of very time-consuming data sets which was successful about 20% of the time.

The other negative aspect of the experiment is that the measured transition energy does not match published values. Our best value was 16269.33 ± .001 cm\textsuperscript{-1} and the most recent published value, which was taken using ion beam methods, is 16269.4408(54) cm\textsuperscript{-1} [1]. Disagreement is likely due to two reasons. The first is the measurement error of our experimental apparatus. This error is likely either due to a combination of the excess ion problem, the system not having sufficient warm up time, or the cause of the high error on the ion measurements. The second reason is the fitting program had trouble fitting to the data because of the small range of the data.
FUTURE WORK

In the course of this experiment, several other possible avenues of investigation were considered. Due to the length and difficulty of collecting data for the experiment described in this thesis, these other avenues were left as future projects.

In order to try to reduce the errors and give a better signal, the first step should be to try to improve the set up. One way to simplify the system would be to find a way to remove the cascode and use only the lock-in amplifier to receive data. It would seem that the more simple the set up, the smaller the probability of error accumulating. The cascode is a highly tuned amplifier, which is the purpose of the input electronics of the lock-in amplifier, seemingly making the cascode redundant. When the cascode is removed, however, we have been unable to find a signal.

The LabVIEW program which controls the experiment might be able to be optimized, as well. The LabVIEW code is very complicated and there are portions which could be improved. For example, the virtual instrument that controls the blast stage could be improved by integrating the updated DAQmx drivers. In general, any possible simplifications of the code will lower the chance of something going wrong.

Future experiments might include trying photodetachment at the corresponding $^2P_{1/2} \rightarrow ^3P_2$ state of the O$^-$ ion. This should be simpler since oxygen tends to give a higher signal when trapped and therefore a higher signal to noise ratio. The $^2P_{1/2} \rightarrow ^3P_2$ threshold of the oxygen ion at 11607.596(18) cm$^{-1}$ should be able to be probed using the Titanium-
Sapphire set up with the ring laser [2]. Oxygen has a smaller fine structure interval than the sulfur ion. Assuming the ions are in equilibrium in the trap, and using the most probable ion velocity, a greater proportion of the ions are in the upper state (28% compared to 19% of sulfur ions). This means that the amount of detachment will be greater and, hopefully, the data fitting program will give better fits.

The experiments for oxygen and sulfur can be repeated using sigma polarized light. Sigma polarized light has a different set of allowed transitions which can be probed. Unfortunately, there are more transitions which are closer together and will therefore be more difficult to resolve.

Another future possibility would be to cool the ions, using evaporative cooling, which would give the Zeeman transition more definition by minimizing thermal broadening. The thermal broadening is accounted for in the fitting program and, using the most probable velocity at 16269.00 cm\(^{-1}\), is on the order of .04 cm\(^{-1}\).

A second potential experiment which would give higher resolution of the Zeeman transitions would be to increase the magnetic field. The Zeeman shifts are dependent on the magnetic field strength, so at a higher field the Zeeman levels are shifted further apart. Our current magnet can reach field strengths of up to 2 Tesla. This would provide shifts 7 times larger than observed in this investigation.
If Zeeman levels can be clearly detected, then the relative transition strengths can be measured. These can then be compared to previous results [12]. More accurate and precise values for the relative transition strengths will allow a more accurate BIL theory.
### Appendix A: Allowed Zeeman Transitions for \( \pi \) and \( \sigma \) Polarized Light

<table>
<thead>
<tr>
<th>Polarization</th>
<th>Initial Z Component of Angular Momentum of Ion</th>
<th>Final Z Component of Angular Momentum of Neutral Atom</th>
<th>Initial Z Component of Angular Momentum of Electron</th>
<th>Shift for n=0 cyclotron state (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \pi )</td>
<td>( \frac{1}{2} )</td>
<td>1</td>
<td>- ( \frac{1}{2} )</td>
<td>0.545</td>
</tr>
<tr>
<td>( \pi )</td>
<td>( \frac{1}{2} )</td>
<td>0</td>
<td>( \frac{1}{2} )</td>
<td>0.778</td>
</tr>
<tr>
<td>( \pi )</td>
<td>- ( \frac{1}{2} )</td>
<td>0</td>
<td>- ( \frac{1}{2} )</td>
<td>0.156</td>
</tr>
<tr>
<td>( \pi )</td>
<td>- ( \frac{1}{2} )</td>
<td>-1</td>
<td>( \frac{1}{2} )</td>
<td>0.389</td>
</tr>
</tbody>
</table>

| \( \sigma \) | \( \frac{1}{2} \)                          | 2                                                 | - \( \frac{1}{2} \)                             | 1.245                                 |
| \( \sigma \) | \( \frac{1}{2} \)                          | 1                                                 | \( \frac{1}{2} \)                              | 1.479                                 |
| \( \sigma \) | \( \frac{1}{2} \)                          | 0                                                 | - \( \frac{1}{2} \)                             | -0.156                                |
| \( \sigma \) | \( \frac{1}{2} \)                          | -1                                                | \( \frac{1}{2} \)                              | 0.078                                 |
| \( \sigma \) | - \( \frac{1}{2} \)                       | 1                                                 | - \( \frac{1}{2} \)                             | 0.856                                 |
| \( \sigma \) | - \( \frac{1}{2} \)                       | 0                                                 | \( \frac{1}{2} \)                              | 1.090                                 |
| \( \sigma \) | - \( \frac{1}{2} \)                       | -1                                                | - \( \frac{1}{2} \)                             | -0.545                                |
| \( \sigma \) | - \( \frac{1}{2} \)                       | -2                                                | \( \frac{1}{2} \)                              | -0.311                                |

The allowed transitions are those which satisfy the following angular momentum conservation equation: \( q + m'' = m' + m_e \). The polarization of the light, \( q \), is either 0 for \( \pi \) polarized light and \( \pm 1 \) for \( \sigma \) polarized light. The \( z \) components of the angular momenta of the ion, the neutral atom and the electron are given by \( m'' \), \( m' \) and \( m_e \), respectively. The energy shift is determined by \( E = EA + \mu B [g'_m m + g'_e m_e + 2N + 1] \). \( EA \) stands for the field free transition threshold, the \( g \)’s are the corresponding Landé g factors and \( N \) is the cyclotron level quantum number \([4], [18]\).
Appendix B: Control Settings for the Included Data Runs

<table>
<thead>
<tr>
<th></th>
<th>29-Jan</th>
<th>30-Aug</th>
<th>10-Aug</th>
<th>14-Jul</th>
</tr>
</thead>
<tbody>
<tr>
<td>FV</td>
<td>-2</td>
<td>-2</td>
<td>-2</td>
<td>-2</td>
</tr>
<tr>
<td>Mass</td>
<td>-306</td>
<td>-306</td>
<td>-306</td>
<td>-305</td>
</tr>
<tr>
<td>BL</td>
<td>700</td>
<td>529</td>
<td>650</td>
<td>400</td>
</tr>
<tr>
<td>INTG</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1200</td>
</tr>
<tr>
<td>VZ2</td>
<td>-2.98583</td>
<td>-2.98583</td>
<td>-2.98583</td>
<td>-2.98583</td>
</tr>
<tr>
<td>FI</td>
<td>6900</td>
<td>6900</td>
<td>6900</td>
<td>6900</td>
</tr>
<tr>
<td>FZ</td>
<td>188</td>
<td>188</td>
<td>188</td>
<td>188</td>
</tr>
<tr>
<td>Empty_V</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Lock-in Amplifier Settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC GAIN</td>
<td>34 dB</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>200 µV</td>
</tr>
<tr>
<td>Time Constant</td>
<td>20ms</td>
</tr>
<tr>
<td>Phase</td>
<td>84.81</td>
</tr>
<tr>
<td>Osc. Freq</td>
<td>188530V</td>
</tr>
<tr>
<td>Osc. Amp</td>
<td>0.055</td>
</tr>
</tbody>
</table>

**FV**: Fill voltage is the DC trapping potential on the trap while it is being filled.

**Mass**: Related to the mass of the ion, it plays a role in determining trap depth.

**BL**: Blast is the total delay in milliseconds between the before blast measurement and the after blast measurement.

**BLCT**: The amount of time that the ensemble was exposed to the laser. It is always at least 10 milliseconds shorter than BL.

**INTG**: The amount of integrated light flux before the shutter is closed during the blast cycle.

**VZ2**: The DC trapping potential of the well.

**FI**: The time the program allows the trap to fill in milliseconds.

**Empty_V**: The voltage used to clear the trap after each run.

**Filament**: 10 times the filament current in amps.
**Fill Bias**: Bias on the filament during the fill stage in volts.

**Wait Bias**: Bias on the filament when it is not creating ions in volts.

**AC Gain**: Sets the gain of the filters and amplifiers of the Lock-in in units of decibels. It should be set as high as possible without overloading the input.

**Sensitivity**: The full scale voltage of the lock-in amplifier.

**Time Constant**: Sets the time constant of the output filters of the lock-in.

**Phase**: Phase shift applied to the reference signal to eliminate any phase shift between it and the input signal.

**Osc. Freq**: The RF frequency, in hertz, applied to the trap drive the oscillations of the ion cloud.

**Osc. Amp**: The amplitude of the driving signal in volts.
Appendix C: Fitting Programs

VCUR

$DEBUG
C      PROGRAM: VCUR.FOR
C      MAIN PROGRAM FOR FITS TAKEN FROM BEVINGTON. WRITTEN BY
C      EA HESSELS. OUTPUT FOR GRAPHS IS SUITABLE FOR GRAFSYS.
C
DIMENSION X(1000), Y(1000), SIGMAY(1000), A(60),
            YFIT(1000), SIGMAA(60), FLT(60), IFL(60)
REAL*8 A, CHISQR
CHARACTER*15 DFILE, PFILE, FITF
DISP = 1
4     NPTS = 1
YMIN = 0.
NIT = 0
OPEN(23, FILE='VCUR.OUT', STATUS='NEW')
WRITE(*,*) 'ENTER THE DATA FILE NAME'
READ(*,7) DFILE
7     FORMAT(A15)
WRITE(*,*) 'ENTER THE PARAMETER FILE NAME'
READ(*,7) PFILE
OPEN(20, FILE =DFILE, STATUS = 'OLD')
1     READ(20,79,IOSTAT=IFEND) X(NPTS), Y(NPTS), SIGMAY(NPTS)
IF(IFEND.LT.0) GOTO 10
WRITE(*,*) X(NPTS),Y(NPTS),SIGMAY(NPTS)
79    FORMAT(3F12.6)
IF(NPTS.EQ.1) THEN
XMIN = X(1)
XMAX = X(1)
ENDIF
IF(XMAX.LE.X(NPTS)) XMAX=X(NPTS)
IF(XMIN.GE.X(NPTS).AND.X(NPTS).NE.0.0) XMIN=X(NPTS)
NPTS = NPTS +1
GO TO 1
10   NPTS = NPTS-1
WRITE(*,*) 'NPTS=',NPTS
CLOSE(20, STATUS='KEEP')
OPEN(20, FILE=DFILE, STATUS = 'OLD', ACCESS='SEQUENTIAL',
+ FORM='FORMATTED')
READ(20,80) NTERMS
80   FORMAT(I3)
READ(20,46) (A(I), FLT(I), I = 1, NTERMS)
46   FORMAT(2F12.6)
NFL = 0
DO 347 I=1,NTERMS
IF(FLT(I).GT..5) THEN
NFL = NFL+1
IFL(NFL) = I
ENDIF
347 CONTINUE
FLAMBDA = .001
GO TO 652
3 CALL CURFIT(X, Y, SIGMAY, NPTS, NFL, IFL, NTERMS, A, SIGMAA, FLAMBDA,
            YFIT, CHISQR)
782 DO 77 I = 1, NTERMS
IF(DISP .EQ. 1.0 .AND. SIGMAA(I) .EQ. 0.0) GO TO 77
WRITE(*,*) I, A(I), SIGMAA(I)
WRITE(23,791) I, A(I), SIGMAA(I)
791 FORMAT(1X,I2,2X,D14.7,2X,E14.7)
77 CONTINUE
$LARGE$

C SUBROUTINE NAME: CFT7.FOR
C PROGRAM TO DO A LEAST SQ FIT TO A NON-LINEAR FUNCTION
C WITH A LINEARIZATION OF THE FITTING FUNCTION. TAKEN
C FROM BEVINGTON P. 237-238 BY EAH.
C
C SUBROUTINE CURFIT(X, Y, SIGMAY, NPTS, NFL, IFL, NTERMS, A,
# SIGMAA, FLAMBDAA, YFIT, CHISQR)
REAL*8 ARRAY, A, FCN, SIGMAA, CHISQR, CHISQ1, B, DET
DIMENSION X(1000), Y(1000), SIGMAY(1000), YFIT(1000), CHISQR
# SIGMAA(60), YFIT(1000), IFL(60)
DIMENSION WEIGHT(1000), ALPHAA(60, 60), BETA(60, 60), DERIV(60),
# ARRAY(60, 60), B(60)
C NFL = NUMBER OF PARAMETERS TO BE "FLOATED"
11        NFREE=NPTS-NFL
13        IF(NFREE)13,13,20
15        CHISQ=0.
16    GO TO 110

C EVALUATE WEIGHTS
20    DO 30 I = 1, NPTS
21        WEIGHT(I)=1./SIGMAY(I)**2
22    CONTINUE

C EVALUATE ALPHA AND BETA MATRICES
C ALPHA AND BETA ARE "CURVATURE" MATRICES OF CHI SQUARE
C SEE P.224 BEVINGTON.
31    DO 34 J = 1, NFL
32        BETA(J)=0.
34    DO 34 K = 1, J
35        ALPHA(J,K) = 0.
38    CONTINUE

C EVALUATE CHI SQUARE FOR THE STARTING POINT
61    DO 62 I = 1,NPTS
62        YFIT(I)=FUNCTN(X,I,A)
63        CHISQ1=FCHISQ(Y,SIGMAY,NPTS,NFREE,YFIT)

C INVERT MODIFIED CURVATURE MATRIX TO FIND NEW PARAMETERS
71    DO 74 J = 1, NFL
72        DO 73 K = 1, NFL
73            ARRAY(J,K)=ALPHA(J,K)/SQRT(ALPHA(J,J)*ALPHA(K,K))
74    CONTINUE
75    CALL MATINV(ARRAY,NFL,DET)
76    IF(DABS(DET).LT.1.D-10)WRITE(*,*)'DETERMINANT IS ZERO'
77    WRITE(*,*)'DETERMINANT IS:', DET
78    DO 893 KKK = 1, NTERMS
79        B(KKK)=A(KKK)
80    DO 84 J = 1, NFL
81        DO 84 K = 1, NFL
82            B(IFL(J))=B(IFL(J))+BETA(J)*ARRAY(J,K)
83                /SQRT(ALPHA(J,J)*ALPHA(K,K))
84    CONTINUE

C IF CHI SQ INCREASES, INCREASE FLAMBDA AND TRY AGAIN
91    DO 92 I = 1, NPTS
92        YFIT(I)=FUNCTN(X,I,B)
93    IF(REAL(CHISQ1-CHISQR))101,101,101
95        FLAMBDA = 10.*FLAMBDA
96    GO TO 71

C EVALUATE PARAMETERS AND UNCERTAINTIES
101   DO 103 J = 1, NFL
102        A(IFL(J))=B(IFL(J))
103    SIGMAA(IFL(J))=SQRT(ARRAY(J,J)/ALPHA(J,J))
104    FLAMBDA = 0.0
105    RETURN
SUBROUTINE MATINV(ARRAY, NORDER, DET)

DOUBLE PRECISION Array, AMAX, SAVE, DET
DIMENSION Array(60,60), IK(60), JK(60)

10 DET=1.
11 DO 100 K = 1, NORDER
   AMAX = 0.
21 DO 30 I=K, NORDER
      DO 30 J=K, NORDER
23 IF(DABS(AMAX)-DABS(ARRAY(I,J)))24,24,30
24 AMAX=ARRAY(I,J)
   IK(K) =I
   JK(K) =J
30 CONTINUE
31 IF (AMAX) 41, 32, 41
32 DET=0.
GO TO 140
41 I = IK(K)
   IF (I-K) 21, 51, 43
43 DO 50 J =1, NORDER
   SAVE = ARRAY(K,J)
   ARRAY(K,J) = ARRAY(I,J)
50 ARRAY(I,J) = -SAVE
51 J = JK(K)
   IF (J-K) 21, 61, 53
53 DO 60 I =1, NORDER
   SAVE = ARRAY(I,K)
   ARRAY(I,K) =ARRAY(I,J)
60 ARRAY(I,J) = -SAVE
61 DO 70 I =1, NORDER
   IF (I-K) 63, 70, 63
63 ARRAY(I,K) =ARRAY(I,K) / AMAX
70 CONTINUE
71 DO 80 I =1, NORDER
   DO 80 J =1, NORDER
   IF (I-K)74, 80, 74
74 IF (J-K) 74, 80, 74
75 ARRAY(I,J) =ARRAY(I,J) +ARRAY(I,K) * ARRAY(K,J)
80 CONTINUE
81 DO 90 J =1, NORDER
   IF (J-K) 83, 90, 83
83 ARRAY(K,J) = ARRAY(K,J) / AMAX
90 CONTINUE
90 ARRAY(K,K) = 1./AMAX
100 DET=DET*AMAX
101 DO 110 L =1, NORDER
   K=NORDER - L + 1
   J = IK(K)
   IF (J-K) 111, 111, 105
105 DO 110 I =1, NORDER
   SAVE = ARRAY(I,K)
   ARRAY(I,K) = -ARRAY(I,J)
110 ARRAY(I,J) = SAVE
111 I = JK(K)
   IF (I-K) 130, 130, 113
113 DO 120 J =1, NORDER
   SAVE = ARRAY(K,J)
   ARRAY(K,J) = -ARRAY(I,J)
120 ARRAY(I,J) = SAVE
130 CONTINUE
140 RETURN
END
FUNCTION FUNCTN(X, I, A)
DIMENSION X(1000), A(60)
REAL*8 A
11 XI = X(I)
FUNCTN = FCN(XI, A)
RETURN
END

FUNCTION FCHISQ(Y, SIGMAY, NPTS, NFREE, YFIT)
REAL*8 CHISQR, FCHISQ
DIMENSION Y(1000), SIGMAY(1000), YFIT(1000)
11 CHISQR = 0.D0
12 IF (NFREE) 13, 13, 20
13 FCHISQ = 0.D0
GO TO 40
20 DO 30 I = 1, NPTS
30 CHISQR = CHISQR + ((Y(I) - YFIT(I))/SIGMAY(I))**2
32 FCHISQ=CHISQR/DBLE(NFREE)
40 RETURN
END
This function is written to fit sulphur detachment data taken at the 2P1/2 -> 3P2 threshold.

To be used in conjunction with "VCUR" least squares fitting code. Final output includes convolution with a thermal gaussian, whose width DEV is one of the fitting parameters. Convolution integration occurs over a total width of 6*DEV. This routine does not include the functional derivatives.

Notes:
1) See Blumberg thesis p. 83 for Lande g factors of S, S-.
2) Variables and parameters defined as follows:
   X: wavelength (in wavenumbers) for which the function is desired.
   N: principle quantum number, gives cyclotron level
   EP: photon energy
   FCN: output (detachment ratio, including thermal broadening)
   M0, MF initial, final magnetic quantum numbers
   ME: detached electron magnetic quantum number (+/- 1/2)
   SIGMA: cross section, found by summing contributions from all allowed transitions for given initial state.
   MUB: Bohr magneton x B field
   Q: polarization (pi: Q=0, sigma: Q = +/- 1)
   INTEN: relative intensity for transition
   NP: number of points in convolution integral
   DEV: standard deviation (width) of convolution gaussian, in wavenumbers
   GAM: small parameter used to eliminate singularities in cross sections
   A(40): other input parameters:
   A(1) baseline detachment ratio (fitted)
   A(2) coefficient of detachment (fitted)
   A(3) integrated photon flux (fitted)
   A(4) EA (fitted)
   A(5) DEV (fitted)
   A(6) B field in Teslas
   A(7) Q
   A(8) NP
   A(9) GAM
   A(10) INFLAG, to choose between equal and variable transition intensities
   A(11-12) free
   A(13-34) lookup table of transition intensities
   A(35-40) free

REAL*8 A
REAL N, NP, E, EP, M0, MF, ME, X, DEV, DY
REAL SIGMA, EA, MUB, INTEN, Q, W, WT, INFLAG
INTEGER LIM
DIMENSION A(40), SIG(4)

Initial state is 2P1/2 state, so J0 = 1/2 and initial magnetic quantum numbers are M0 = +1/2, -1/2. Final state is 3P2, so final magnetic quantum numbers are -2, -1, 0, 1, 2. g factor of ion in 2P1/2 state is 2/3 (see Jopson thesis p. 9), g factor of electron is 2 and g factor of neutral atom is 3/2.
EA = A(4)
DEV = A(5)
MUB = 0.467*A(6)
Q = A(7)
NP = A(8)
GAM = A(9)
INFLAG = A(10)
SIG(2) = 0.0
SIG(3) = 0.0
WT = 0.0
DY = 6.0*DEV/(NP-1.0)
LIM = INT((NP-1.0)/2.0)
DO 30 I1 = -LIM,LIM
   EP = X + FLOAT(I1)*DY
   W = EXP(-0.5*((X-EP)/DEV)**2)
   WT = WT + W
DO 40 I2 = 2,3
   M0 = FLOAT(I2) - 2.5
   SIGMA = 0.0
   DO 50 K = 0,5
      N = FLOAT(K)
      DO 60 I3 = -2,2
         MF = FLOAT(I3)
         DO 70 I4 = 0,1
            ME = FLOAT(I4) - 0.5
            E = EA + MUB*(1.5*MF + 2.0*ME - (2.0/3.0)*M0 +
                           2.0*N+1.0)
            IF (E.GE.EP) GOTO 70
            IF (((MF+ME) .NE. (M0+Q)) .AND.
                 (((MF+ME) .NE. (M0-Q))) GOTO 70
               Q = MF + ME - M0
               IF (INFLAG.EQ.0.0) THEN
                  CALL INTENSITY(M0, MF, ME, Q, A, INTEN)
               ELSE
                  INTEN = 1.0
               ENDIF
         70               CONTINUE
      60            CONTINUE
   50         CONTINUE
   SIG(I2) = SIG(I2) + SIGMA*W
30   CONTINUE
SIG(2) = SIG(2)/WT
SIG(3) = SIG(3)/WT
FCN = A(1) + A(2)*(EXP(-SIG(2)*A(3)) + EXP(-SIG(3)*A(3)))
RETURN
END

SUBROUTINE INTENSITY(M0, MF, ME, Q, A, INTEN)
REAL M0, MF, ME, Q, INTEN
REAL*8 A
DIMENSION A(40)
IF (Q .EQ. 0.0) GOTO 10
IF (ABS(Q) .EQ. 1.0) GOTO 20
10   IF ((M0 .EQ. 1.5) .AND. (MF .EQ. 2.0) .AND. (ME .EQ. .5)) THEN
      INTEN=A(13)
   ELSE IF (((M0 .EQ. 1.5) .AND. (MF .EQ. 1.0) .AND. (ME .EQ. 0.5)) THEN
      INTEN=A(14)
   ELSE
      CALL INTENSITY(M0, MF, ME, Q, A, INTEN)
   ENDIF
RETURN
END
ELSE IF ((M0.EQ.0.5).AND.(MF.EQ.1.0).AND.(ME.EQ.-0.5)) THEN
  INTEN=A(15)
ELSE IF ((M0.EQ.0.5).AND.(MF.EQ.0.0).AND.(ME.EQ.0.5)) THEN
  INTEN=A(16)
ELSE IF ((M0.EQ.-0.5).AND.(MF.EQ.0.0).AND.(ME.EQ.-0.5)) THEN
  INTEN=A(17)
ELSE IF ((M0.EQ.-0.5).AND.(MF.EQ.-1.0).AND.(ME.EQ.0.5)) THEN
  INTEN=A(18)
ELSE IF ((M0.EQ.-1.5).AND.(MF.EQ.-2.0).AND.(ME.EQ.0.5)) THEN
  INTEN=A(19)
ELSE IF ((M0.EQ.-1.5).AND.(MF.EQ.-1.0).AND.(ME.EQ.-0.5)) THEN
  INTEN=A(20)
ELSE
  WRITE(*,*) ' ****** Error in selection rule (pi) !!'
ENDIF
GOTO 30

NOTE: Need to fix these weights for 2P1/2 initial state.
Weights below are for 2P3/2 initial state with
sigma polarization,

20   IF ((M0.EQ.1.5).AND.(MF.EQ.0.0).AND.(ME.EQ.0.5).AND.(Q.EQ.-1.0)) THEN
     INTEN=A(21)
ELSE IF ((M0.EQ.1.5).AND.(MF.EQ.2.0).AND.(ME.EQ.0.5).AND.(Q.EQ.1.0)) THEN
     INTEN=A(22)
ELSE IF ((M0.EQ.1.5).AND.(MF.EQ.1.0).AND.(ME.EQ.-0.5).AND.(Q.EQ.1.0)) THEN
     INTEN=A(23)
     INF4 = 1
ELSE IF ((M0.EQ.0.5).AND.(MF.EQ.-1.0).AND.(ME.EQ.0.5).AND.(Q.EQ.-1.0)) THEN
     INTEN=A(24)
ELSE IF ((M0.EQ.0.5).AND.(MF.EQ.1.0).AND.(ME.EQ.0.5).AND.(Q.EQ.1.0)) THEN
     INTEN=A(25)
     INF3 = 1
ELSE IF ((M0.EQ.0.5).AND.(MF.EQ.2.0).AND.(ME.EQ.-0.5).AND.(Q.EQ.1.0)) THEN
     INTEN=A(26)
     INF3 = 1
ELSE IF ((M0.EQ.-0.5).AND.(MF.EQ.-2.0).AND.(ME.EQ.0.5).AND.(Q.EQ.-1.0)) THEN
     INTEN=A(27)
ELSE IF ((M0.EQ.-0.5).AND.(MF.EQ.-1.0).AND.(ME.EQ.-0.5).AND.(Q.EQ.1.0)) THEN
     INTEN=A(28)
     INF2 = 1
ELSE IF ((M0.EQ.-0.5).AND.(MF.EQ.1.0).AND.(ME.EQ.-0.5).AND.(Q.EQ.1.0)) THEN
     INTEN=A(29)
     INF2 = 1
ELSE IF ((M0.EQ.-1.5).AND.(MF.EQ.0.0).AND.(ME.EQ.0.5).AND.(Q.EQ.1.0)) THEN
     INTEN=A(30)
     INF1 = 1
ELSE IF ((M0.EQ.-1.5).AND.(MF.EQ.-1.0).AND.(ME.EQ.0.5).AND.(Q.EQ.1.0)) THEN
     INTEN=A(31)
ELSE IF ((M0.EQ.-1.5).AND.(MF.EQ.-2.0).AND.(ME.EQ.-0.5).AND.(Q.EQ.1.0)) THEN
     INTEN=A(32)
     INF1 = 1
ELSE IF ((M0.EQ.-1.5).AND.(MF.EQ.-1.0).AND.(ME.EQ.-0.5).AND.(Q.EQ.1.0)) THEN
     INTEN=A(33)
     INF1 = 1

55
ELSE IF ((M0.EQ.-1.5).AND.(MF.EQ.0.0).AND.(ME.EQ.-0.5).AND. (Q.EQ.1.0)) THEN
    INTEN=A(34)
ELSE
    WRITE(*,*) ' ****** Error in selection rule (sigma) !! '
    WRITE(*,40) M0, MF, ME, Q
ENDIF

30 CONTINUE
RETURN
END
SUBROUTINE FDERIV(X, IT, A, NPAR, DERIV)

This routine is written to fit sulphur detachment data at the 2P1/2 - 3P2 threshold.

To be used in conjunction with "VCUR" least squares fitting code. Output includes functional derivatives wrt fitted parameters, taking into account convolution with a thermal gaussian, whose width DEV is one of the fitting parameters. Convolution integration occurs over a total width of 6*DEV.

Notes:
1) See Blumberg thesis p. 83 for Lande g factors of S, S-.
2) Variables and parameters defined as follows:
   X: array of points (in wavenumbers) fitted by VCUR
   NPAR: number of parameters (inc. fitted and non-fitted)
   N: principle quantum number, gives cyclotron level
   EP: photon energy
   FCN: output (detachment ratio, including thermal broadening)
   M0, MF initial, final magnetic quantum numbers
   ME: detached electron magnetic quantum number (+/- 1/2)
   SIGMA: cross section, found by summing contributions from all allowed transitions for a given initial state
   MUB: Bohr magneton x B field
   Q: polarization (pi: Q=0, sigma: Q = +/- 1)
   INTEN: relative intensity for transition
   NP: number of points in convolution integral
   DEV: standard deviation (width) of convolution gaussian, in wavenumbers, based on ion cloud temp and laser bandwidth, etc.
   GAM: small parameter used to eliminate singularities in cross sections
   DERIV(40) partial derivatives of FCN wrt fitted parameters
   IT: index passed by VCUR to address wavelength
   A(40): other input parameters:
   A(1) baseline detachment ratio (fitted)
   A(2) coefficient of detachment (fitted)
   A(3) integrated photon flux (fitted)
   A(4) EA (fitted)
   A(5) DEV (fitted)
   A(6) B field in Teslas
   A(7) Q
   A(8) NP
   A(9) GAM
   A(10) INFLAG, to specify equal or variable transition intensities
   A(11-12) free
   A(13-34) lookup table of transition intensities
   A(35-40) free

REAL*8 A
REAL N, NP, E, EP, M0, MF, ME, DEV, DY, INFLAG
REAL SIGMA, EA, MUB, INTEN, Q, W, WT, SDEV, SEA
INTEGER LIM
DIMENSION A(40), SIG(4), DERIV(40), X(1000)
DIMENSION SIGDEV(4), SIGEA(4)
Initial state is 2P1/2 state, so J0 = 1/2 and initial magnetic quantum numbers are +1/2, -1/2. Final state is 3P2, so final magnetic quantum numbers are -2, -1, 0, 1, 2.

DO 80 I = 1, 40
  DERIV(I) = 0.0
80   CONTINUE

EA = A(4)
DEV = A(5)
MUB = 0.467*A(6)
Q = A(7)
NP = A(8)
GAM = A(9)
INFLAG = A(10)

DO 90 I = 2, 3
  SIG(I) = 0.0
  SIGDEV(I) = 0.0
  SIGEA(I) = 0.0
90   CONTINUE

WT = 0.0
DY = 6.0*DEV/(NP-1.0)
LIM = INT((NP-1.0)/2.0)

DO 30 I1 = -LIM, LIM
  EP = X(IT) + FLOAT(I1)*DY
  W = EXP(-0.5*((X(IT) - EP)/DEV)**2)
  WT = WT + W
  DO 40 I2 = 2, 3
    M0 = FLOAT(I2) - 2.5
    SIGMA = 0.0
    SDEV = 0.0
    SEA = 0.0
  40    CONTINUE
  DO 50 K = 0, 5
    N = FLOAT(K)
    DO 60 I3 = -2, 2
      MF = FLOAT(I3)
      DO 70 I4 = 0, 1
        ME = FLOAT(I4) - 0.5
        E = EA + MUB*(1.5*MF + 2.0*ME - (2.0/3.0)*M0 +
        2.0*N+1.0)
      70     IF (E.GE.EP) GOTO 70
      IF (((MF+ME) .NE. (M0+Q)) .AND.
        ((MF+ME) .NE. (M0-Q))) GOTO 70
        Q = MF + ME - M0
      IF (INFLAG.EQ.0.0) THEN
        CALL INTENSITY(M0, MF, ME, Q, A, INTEN)
      ELSE
        INTEN = 1.0
      ENDIF
      SDEV = SDEV + INTEN*6.0*FLOAT(I1)/(NP-1.0) *
      (0.5/(SQRT(EP-E)*(EP-E+GAM)) -
      SEA = SEA + INTEN*
       (0.5/(SQRT(EP-E)*(EP-E+GAM)) +
50   CONTINUE

DO 20 I2 = 2, 3
\[ \text{SIG(I2)} = \frac{\text{SIG(I2)}}{\text{WT}} \]
\[ \text{SIGDEV(I2)} = \frac{\text{SIGDEV(I2)}}{\text{WT}} \]
\[ \text{SIGEA(I2)} = \frac{\text{SIGEA(I2)}}{\text{WT}} \]

20 CONTINUE

FCN = A(1) + A(2) \times (\exp(-\text{SIG(2)} \times A(3)) + \exp(-\text{SIG(3)} \times A(3)))

Calculate partial derivatives of FCN with respect to the
fitted parameters for VCUR.

DERIV(1) = 1.0
DERIV(2) = \exp(-\text{SIG(2)} \times A(3)) + \exp(-\text{SIG(3)} \times A(3))
DERIV(3) = -A(2) \times (\text{SIG(2)} \times \exp(-\text{SIG(2)} \times A(3)) +
\quad \text{SIG(3)} \times \exp(-\text{SIG(3)} \times A(3)))
DERIV(4) = -A(2) \times A(3) \times (\exp(-\text{SIG(2)} \times A(3)) \times \text{SIGEA(2)} +
\quad \exp(-\text{SIG(3)} \times A(3)) \times \text{SIGEA(3)})
DERIV(5) = -A(2) \times A(3) \times (\exp(-\text{SIG(2)} \times A(3)) \times \text{SIGDEV(2)} +
\quad \exp(-\text{SIG(3)} \times A(3)) \times \text{SIGDEV(3)})

RETURN
END
Bibliography


