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Photodetachment spectroscopy from the lowest threshold of S^-

James E. Wells* and J. N. Yukich†

Physics Department, Davidson College, P.O. Box 7133, Davidson, North Carolina 28035-7133, USA

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We have observed the photodetachment spectrum near the lowest detachment threshold from S^- in a 1 T field. The spectroscopy shows a small degree of magnetic field structure of the type observed in similar experiments at the higher-energy threshold of the electron affinity. Furthermore, our results yield a measurement of the lowest detachment threshold energy.

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I. INTRODUCTION

For over 30 years, photodetachment of electrons from negative ions in external magnetic fields has generated considerable experimental and theoretical work [1–8]. The principal effect of a magnetic field is to force the outgoing free-electron wave function to undergo cyclotron orbit. A portion of the outgoing wave function may return to the atomic core, where it can interfere with any residual electron wave function. The cyclotron motion is quantized in the plane perpendicular to the field, and the electron's axial motion along the field axis is continuous [9]. The spectroscopic result of this one-dimensional continuum is a pattern of oscillations in the near-threshold detachment cross section corresponding to the electron's infinite set of Landau levels [1]. The effect has been studied in the frequency domain as well as the time domain [10–12]. The magnetic field also splits the fine-structure levels of the ion, the neutral atom, and the electron. Thus, each Landau threshold is composed of multiple Zeeman thresholds which depend on the initial state(s) of the ion, the final state(s) of the atom, the spin of the electron, and the photon polarization.

Numerous experiments have focused on photodetachment spectroscopy near the *electron affinity*, defined as the energy difference between lowest state of the ion and the lowest state of the neutral atom. In the case of S^-, O^-, and Se^-, this corresponds to the ${}^2P_{3/2} \rightarrow {}^3P_2$ transition, shown as transition A in Fig. 1. Previous work at this transition has resolved the above-mentioned Landau magnetic structure in numerous experiments and in some cases has resolved the individual Zeeman thresholds [1,3–5,12–14]. In most cases, these experiments have shown strong agreement with the theory of Blumberg, Itano, and Larson (hereafter referred to as BIL) [2]. This theory was initially developed to model the photodetachment process in a magnetic field at the electron affinity transition. However, three experiments have uncovered a clear departure from the BIL theory [4,5,14], motivating a more thorough testing of the theory in general.

Detachment spectroscopy at the electron affinity transition is clearly important. However, spectroscopy of the lowest-lying transition, corresponding to detachment from the highest bound state, also yields valuable information about the short-range potential binding the extra electron, as well as values for the spin-orbit splitting. Yet, relatively little work has been conducted at the lowest transition. For example, the only previous experiment to investigate detachment at this transition in a magnetic field failed to detect any structure in the detachment [15].

In this paper we report on an experiment to investigate the validity of the BIL theory to detachment at the lowest threshold of S^-, at the ${}^2P_{1/2} \rightarrow {}^3P_2$ transition, shown as transition B in Fig. 1. The experiment is conducted in a Penning ion trap with a field of 1.0 Tesla. We use a single-mode continuous-wave laser with polarization parallel to the magnetic field (π-polarized light). The long laser interaction time afforded by the ion trap and continuous laser permits relatively precise energy measurements compared to what is achievable with an ion beam. Another distinguishing feature of this experiment is that our choice of laser polarization allows only four individual Zeeman transitions for each Landau level. Thus the overall spectroscopy is expected to be simpler than found in many previous experiments [2,3,12,14,16]. Our re-

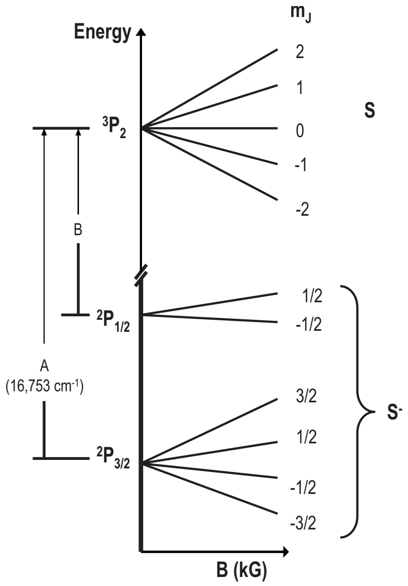

FIG. 1. Level diagram showing splitting of the two bound states of the S^- ion, as well as the ground state of the neutral S atom. Transition A corresponds to the electron affinity and transition B is the focus of the present work.

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*Present address: Department of Physics, University of Connecticut, 2152 Hillside Road, Storrs, CT 06269-3046.

†joyukich@davidson.edu; http://www.phy.davidson.edu/FacHome/jny/welcome.htm

sults show a small degree of structure above the lowest threshold. Furthermore, by fitting the BIL theory to the data we arrive at a value for the energy of the lowest detachment transition. Our result is consistent with the recent value produced by the photodetachment microscope [17], lending further credibility to this method.

II. THEORY

The BIL theory has been described extensively in the literature [2,3], so we will only summarize it here. In the present work, our experiment probes near-threshold *s*-wave detachment at the $^2P_{1/2} \rightarrow {}^3P_2$ transition. The $^2P_{1/2}$ state is the higher of just two bound states (an inverted doublet) of the S$^-$ ion, and the $^3P_2$ state is the ground state of the neutral atom, part of an inverted triplet. In the absence of a magnetic field, the detachment could be described by the Wigner law [18]. Presence of a magnetic field splits the $^2P_{1/2}$ and $^3P_2$ states into their magnetic Zeeman sublevels, but the dominant effect of the field is to constrain motion of the electron to quantized cyclotron levels. Thus, the magnetic field brings about periodic discontinuities, spaced by the cyclotron frequency, in the density of final states. According to Fermi's golden rule, this periodic variation in the density of final states gives rise to periodic structure in the detachment cross section. Each cyclotron level has a threshold given in the ion's frame by

$$\hbar\omega = \hbar\omega_0 + \hbar\omega_c(n + 1/2), \tag{1}$$

where ω is the light frequency, n is the principal quantum number of the Landau level, ω_c is the cyclotron frequency, and $\hbar\omega_0$ is the zero-field threshold. The detached electron's total energy in the one-dimensional continuum is

$$E = \hbar\omega_0 + \hbar\omega_c(n + 1/2) + \frac{p_z^2}{2m}, \tag{2}$$

where p_z is the electron's momentum along the field axis [2,3].

For each Landau level of the detached electron, there are 12 possible Zeeman thresholds within a total range of $\approx 4.33\mu_B B$. Relative to the zero-field threshold, the Zeeman threshold energies are given by

$$E_{if} = \mu_B B(g_f m_f + g_e m_e - g_i m_i + 2n + 1), \tag{3}$$

where μ_B is the Bohr magneton. The g-factors g_f, g_e, and g_i refer to the $^3P_2$ state of the neutral atom, the electron, and the $^2P_{1/2}$ state of the ion, respectively. The magnetic quantum numbers m_f, m_e, and m_i are similarly defined. As shown in Table I eight of these Zeeman transitions occur with σ-polarized light ($q = \pm 1$) and four with π-polarized light ($q = 0$), and the four π thresholds span a range of only $(4/3)\mu_B B$. The allowed Zeeman transitions are those that satisfy the selection rule $m_i + q = m_f + m_e$. Assuming *LS* coupling, the Wigner-Eckart theorem and the Wigner 3-*j* and 6-*j* symbols allow us to calculate the relative strengths of these transitions [16]. In the case of π-polarized light, as used in our experiment, these relative strengths vary only by 50% among the four allowed transitions.

TABLE I. Details of the allowed Zeeman transitions between the sublevels of $^2P_{1/2}$ in S$^-$ and $^3P_2$ in neutral S. The fifth column denotes the relative weight factor. The sixth column gives the frequency shift in units of $\mu_B B$ relative to the zero-field threshold.

q	m_i	m_f	m_e	Weight	ΔE_{if}
1	$\frac{1}{2}$	2	$-\frac{1}{2}$	12	+1.667
1	$\frac{1}{2}$	1	$\frac{1}{2}$	3	+2.167
−1	$\frac{1}{2}$	−1	$\frac{1}{2}$	3	−0.833
−1	$\frac{1}{2}$	0	$-\frac{1}{2}$	2	−1.333
0	$\frac{1}{2}$	1	$-\frac{1}{2}$	6	+0.167
0	$\frac{1}{2}$	0	$\frac{1}{2}$	4	+0.667
0	$-\frac{1}{2}$	0	$-\frac{1}{2}$	6	−0.667
0	$-\frac{1}{2}$	−1	$\frac{1}{2}$	4	−0.167
1	$-\frac{1}{2}$	0	$\frac{1}{2}$	2	+1.333
1	$-\frac{1}{2}$	1	$-\frac{1}{2}$	3	+0.833
−1	$-\frac{1}{2}$	−1	$-\frac{1}{2}$	3	−2.167
−1	$-\frac{1}{2}$	2	$\frac{1}{2}$	12	−1.667

The partial cross section found at each threshold is given by

$$\sigma(k) \propto \frac{4k}{\gamma^2 + 4k^2}. \tag{4}$$

Here, k is the wave number corresponding to p_z, and γ is a constant proportional to the depth of a possible short-range final-state interaction between the electron and the atomic core [3]. Each partial cross section is weighted by the appropriate Zeeman transition strength. In our experiment, we measure the percentage of ions surviving photodetachment in the ion trap. The ions are assumed to populate the magnetic sublevels of the initial $^2P_{1/2}$ state in a Boltzman distribution. The fraction of ions surviving illumination is related to the photodetachment cross section by $F(\nu) = \Sigma_i f_i e^{-A\sigma_i(\nu)}$, where f_i is the relative population of the ith initial state, A is proportional to the total optical flux during the laser interaction time, and $\sigma_i(\nu)$ is the cross section for detachment from the ith initial state. The total cross section for a given photon energy is the sum of all the partial cross sections corresponding to the allowed Zeeman transitions and all Landau levels allowed by energy conservation [2]. To account for thermal broadening effects, the fitting procedure includes convolution with a Gaussian function whose width is one of the fit parameters. Other fit parameters include the field-free detachment threshold.

III. EXPERIMENTAL TECHNIQUE

The apparatus and experimental technique used in this work have been described previously [1–3,12,16], so we give a brief overview here. Our photodetachment spectroscopy is conducted by observing the depletion of ions stored in a Penning ion trap when the ions are illuminated by a tunable single-mode laser. We create the ions in the Penning trap by dissociative attachment to a carrier gas controlled by a variable leak [19]. In the case of S$^-$, we use a carrier gas of carbonyl sulfide (OCS) at a pressure of approximately 3×10^{-8} Torr. The ultrahigh vacuum system has a background pressure of approximately 5×10^{-10} Torr. Each experiment

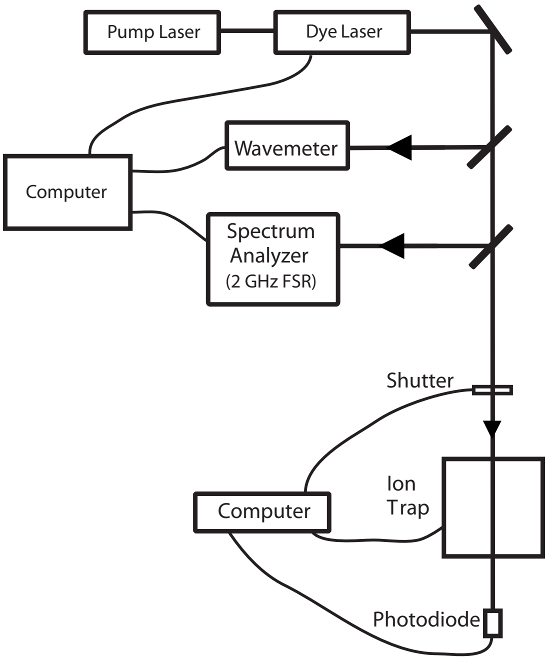

FIG. 2. Schematic diagram of the major optical apparatus and the ion trap. The ions undergo photodetachment with light from a tunable, single-mode, dye ring laser. A computer-controlled mechanical shutter maintains a constant optical flux, measured by the photodiode, from cycle to cycle of the data acquisition.

is performed with an ensemble on the order of 10^4 ions. We make a relative measurement of the number of trapped ions by driving the ions' resonant axial motion with a radio frequency voltage applied to the trap endcaps. The image current induced on the trap ring electrode is detected at twice the driving frequency by a tuned coil. The resulting voltage is amplified with a highly tuned preamplifier and then detected with a commercial high-frequency lock-in amplifier [2].

The ions are illuminated with light from a tunable, single longitudinal mode ring dye laser operated with Kiton Red dye, shown in Fig. 2. The laser is tuned with a birefringent filter and two etalons to produce the 614 nm light needed to photodetach the S^- ions. The laser wavelength is determined by a wavelength meter and a Fabry-Perot spectrum analyzer. The laser beam is aligned through the ion trap and the transmitted flux is recorded by a photodiode. A feedback signal from the photodiode to a mechanical shutter maintains constant integrated light flux from cycle to cycle of the experiment.

One cycle of data acquisition consists of a background noise measurement by the ion detection electronics, followed by an ion creation period, an initial ion signal measurement, an optical interaction period, and a final ion signal measurement. The ratio of the two ion signal measurements gives the fraction of ions surviving the interaction time. To account for trap losses by mechanisms other than detachment, alternate data cycles measure the trap retention ratio in the absence of laser light (shutter closed). Thus the ratio of the fraction of ions surviving the interaction period with and without light yields a fraction of ions surviving photodetachment, corrected to first order for background losses. The model described in Sec. II is then fit to the data with the adjustable parameters.

Toward the beginning of the experiment we encountered a difficulty known as the "excess ion" problem. This is the name given to the phenomenon of an apparent net increase in the number of ions during the laser illumination period. The result is a fraction of ions surviving photodetachment that can exceed 1.0. Indeed, this problem was observed during the first experiments on negative ion detachment in a magnetic field [15]. It is thought to be caused by production of S_2^- during the ion creation period through the reaction $S^- + OCS \to S_2^- + CO$. The detachment threshold for S_2^- has been experimentally found to be 1.670 eV [20], or fully 0.35 eV lower than the S^- lowest threshold. Thus, any S_2^- population produced in the trap will be photodetached, yielding 0.35 eV electrons which in turn produce further S^- ions by dissociative attachment

$$h\nu + S_2^- \to e^- + S_2$$

$$e^- + OCS \to S^- + CO. \qquad (5)$$

If this process occurs at a rate faster than detachment from S^-, then the number of S^- ions in the trap will increase during the laser illumination period rather than decrease. We found that this behavior could be greatly diminished by purging the trap of S_2^- prior to making any S^- measurements. The purging is accomplished by applying to the trap end caps a radio frequency potential tuned to the resonant axial motion of S_2^-.

IV. RESULTS AND DISCUSSION

In our experiment, multiple sets of data were acquired to determine the ratio of ions surviving detachment for photon energies near the ${}^2P_{1/2} \to {}^3P_2$ threshold of S^-. The magnetic field was set at 1.0 Tesla. In each data run, π-polarized laser light was used in order to maximize the possibility of resolving the individual Zeeman thresholds. The laser bandwidth varied under 300 MHz, narrow compared to other motional broadening mechanisms such as the motional Stark effect and Doppler broadening. Figure 3 shows an example of the results. Fluctuations in the ion trap conditions, which can manifest themselves over the long periods required to acquire the data, prohibit collecting data over more than a couple of wave numbers.

Shown in Fig. 3 is a theoretical fit to the model described in Sec. II. The initial threshold is evident; however, the multiple Zeeman thresholds are unresolved. The spacing between Zeeman thresholds at 1.0 T averages 0.21 cm^{-1}; a combination of motional broadening and the density of data points makes it very difficult to resolve these thresholds. We also note that due to the relatively large spin-orbit splitting in S^-, we have a very small initial population in the ${}^2P_{1/2}$ state. This reduces our signal to noise ratio compared to that found in previous experiments at the electron affinity threshold. Thus, while evaporative cooling would reduce thermal broadening, it would also further diminish the population in the ${}^2P_{1/2}$ initial state. However, efforts are underway to increase the magnetic field, which will increase spacing between the Zeeman thresholds in future experiments.

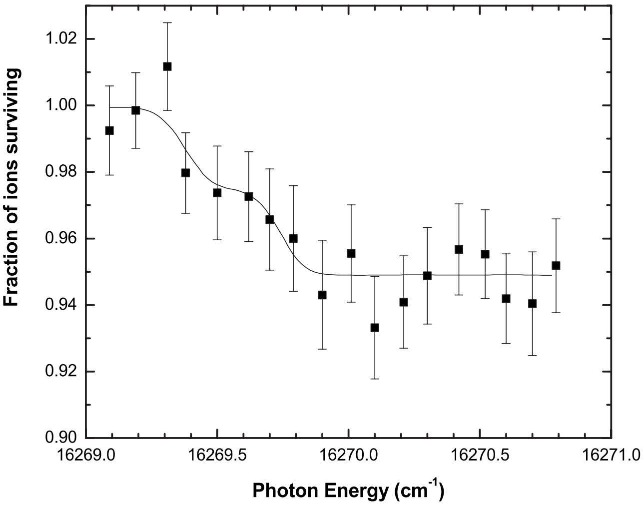

FIG. 3. Photodetachment data at the $^2P_{1/2} \rightarrow {}^3P_2$ threshold of S$^-$. The fraction of ions surviving laser illumination is plotted as a function of photon energy. The data shown are for a field of 1.0 T and π-polarized light. The solid curve shows a fit to the data from which is derived a measure of the field-free detachment threshold.

The fit to the theoretical model yields a value for the lowest S$^-$ detachment threshold of 16269.380(88) cm^{-1}. This is compatible with the recently measured value of 16269.4410(45) cm^{-1} using the photodetachment microscope method [17]. Our total uncertainty of 0.088 cm^{-1} is comprised of three uncertainties. The first is an instrumental uncertainty of 0.012 cm^{-1} from the wavelength meter; this is an absolute uncertainty to three standard deviations. The second uncertainty is a standard deviation of 0.033 cm^{-1} from the theoretical fit of the model to the data. To state a full confidence interval, we multiply this standard deviation by a large confidence factor of 2.0, yielding a statistical uncertainty of 0.066 cm^{-1}. Lastly, we account for possible systematic error due to the magnetic field, which is measured to within 0.01 T. By allowing the field to vary between 0.99 and 1.01 T and repeating the model fitting, we find an average possible deviation of 0.010 cm^{-1}. There may be some overlap of these uncertainties, but we take the linear sum of these three uncertainties as the outside limit of the total possible uncertainty, or 0.088 cm^{-1}. This error bar gives a full confidence interval.

We note several differences in the current data from results of previous experiments conducted at the $^2P_{3/2} \rightarrow {}^3P_2$ transition [1,12,14,16]. First, the overall degree of detachment (as indicated by 100% minus the fraction of ions surviving detachment) is lower than in the previous work cited above. This is to be expected, however, given the relatively large spin-orbit splitting of the S$^-$ ion. Second, the data do not show cyclotron structure as clearly as we have frequently found near the electron affinity. We believe that this diminished magnetic-field structure is due to the reduced signal to noise ratio.

We also note in Fig. 3 some residual excess ion effect visible below the initial threshold. However, we are confident that this effect has not influenced the overall spectroscopy. For photon energies fully 0.35 eV higher than the S$_2^-$ threshold, we expect detachment from S$_2^-$ to be energy independent. Thus, any artificial increase in the S$^-$ detachment ratio due to the excess ion effect should be a uniform offset and not impact measurement of the $^2P_{1/2} \rightarrow {}^3P_2$ threshold.

V. CONCLUSIONS

Frequency-domain spectra of photodetachment in a magnetic field at the lowest threshold from S$^-$ have been observed using π-polarized laser light. Theoretical fits to the data yield a threshold energy of 16269.380(88) cm^{-1}. This measurement is compatible with a recent value by the photodetachment microscope method and reinforces that method and its result. Our larger uncertainty suggests further efforts to improve the overall signal quality. Future experiments will examine detachment from the lowest threshold of other ions whose spin-orbit splitting is smaller. Furthermore, an increase in the ion trap's magnetic field may allow us to resolve the individual Zeeman thresholds and measure their relative transition strengths.

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