PHYSICAL REVIEW A **93**, 023431 (2016)

Vibrational photodetachment spectroscopy near the electron affinity of S_2

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(Received 21 December 2015; published 26 February 2016)

We have conducted laser photodetachment spectroscopy near the detachment threshold of the electron affinity of S_2 in a 1.8-T field. The ions are prepared by dissociative electron attachment to carbonyl sulfide. The experiment is conducted in a Penning ion trap and with a narrow-band, tunable, Ti:sapphire laser. A hybrid model for photodetachment in an ion trap is fit to the data using the appropriate Franck-Condon factors. The observations reveal detachment from and to the first few vibrational levels of the anion and the neutral molecule, respectively. Evaporative cooling of the anion ensemble condenses the thermal distribution to the lowest initial vibrational states. The subsequent detachment spectroscopy yields results consistent with a vibrationally cooled anion population.

DOI: 10.1103/PhysRevA.93.023431

I. INTRODUCTION

For many decades photodetachment spectroscopy has been employed to develop fundamental understanding of atomic and molecular structure and interactions. Such studies in the area of single-atom negative ions have provided measurements of electron affinities, other threshold energies, spin-orbit splittings, *g* factors, and a variety of transition strengths. Photodetachment spectroscopy conducted in the presence of external electric and magnetic fields has allowed further tests of atomic and molecular theories and models. The presence of an external field causes a portion of the outgoing electronic wave function to return to the atomic core, where it may then interfere with any subsequent wave function. The detachment process essentially becomes an interferometer whose effects are often manifested as periodic structure in the photodetachment cross section. In a magnetic field, this structure includes the effects of the outgoing electron's cyclotron motion, as well as the Zeeman effect [1–14]. Experiments in single-atom photodetachment spectroscopy have employed a variety of techniques including photoelectron spectroscopy, laser photodetachment threshold spectroscopy, and photodetachment microscopy. In particular, experiments investigating *s*-wave detachment have produced very high precision spectroscopy due to the sharp onset of the Wigner cross section at threshold. Several of these experiments have successfully employed the theory of Blumberg, Itano, and Larson (hereafter referred to as BIL) to study single-atom detachment spectroscopy in a Penning ion trap [1–3,10,12–16]. In the case of molecular anions, additional structure in the detachment cross section is generally expected due to the molecule's rotational and vibrational degrees of freedom. The same kinds of spectroscopic techniques have been used to investigate molecular photodetachment, resulting in measurements of electron affinities, rotational and vibrational constants, and transition strengths. Some of these experiments have also been conducted in the presence of external fields [15–23].

In this paper we report on an experiment conducted to observe the photodetachment spectroscopy of the $S_2{}^-$ anion. Previous investigations of this anion have focused on detachment at or above the electron affinity, and have used photoelectron spectroscopy. These experiments have yielded values for the electron affinity of S_2 as well as vibrational energies [22,23]. Our experiment investigates detachment both above and below the electron affinity with a total range of approximately 2000 cm^{-1}, and is conducted with laser photodetachment spectroscopy using a narrow-band, tunable Ti:sapphire laser. The ions are prepared, trapped, and stored in a Penning ion trap, whose long storage times generally permit relatively high precision energy measurements. Although our apparatus lacks discrimination of photoelectron energies, it does offer resolution of the relative detachment probability [1,2,10,13,14]. The anions are created using a two-step process of dissociative electron attachment to carbonyl sulfide [24]. Our spectroscopy includes detachment from both of the ${}^2\Pi_g$ electronic states of the anion into the ${}^3\Sigma_g^-$ state of the neutral molecule. We model the detachment as a vibrational transition between two harmonic oscillators. Because the anion sample is relatively energetic, several excited vibrational levels of each electronic ground state are occupied. Although the BIL theory has generally been successful with modeling detachment from trapped single-atom ions, it has never been used to study detachment from homonuclear anions. In this paper we numerically model photodetachment from $S_2{}^-$ by merging the BIL model with the cross section for detachment from a diatomic anion derived by Geltman [2,25]. This hybrid model, including the appropriate Franck-Condon factors, is shown to be compatible with several sets of data, and the model shows that the anions are formed in a thermal distribution of the four lowest vibrational states of both electronic ground states. Finally, by evaporatively cooling the ions prepared in the trap we are able to reduce the overall vibrational distribution of initial states. Evidence of thermal redistribution of the initial

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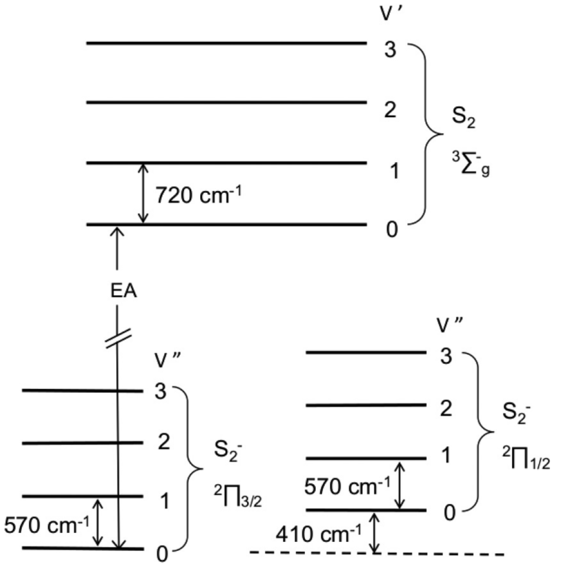

FIG. 1. Vibrational energy levels of the two electronic ground states of the $S_2{}^-$ anion and the electronic ground state of the neutral.

vibrational states is observed. These results corroborate the correlation between ion trap well depth and average energy of the trapped ion species [26]. Our results also prompt further studies with higher energy resolution and further studies with other diatomic anions.

II. THEORY

Our experiment uses tunable laser light to probe photodetachment both above and below the recommended electron affinity of S_2. As shown in Fig. 1, the neutral molecule has a $^3\Sigma^-_g$ ground state, analogous to that of molecular oxygen. The neutral also has an excited $^1\Delta_g$ state; several theoretical predictions and laboratory measurements indicate that this excited state should be at least 4000 cm^{-1} above the ground state [23,27], outside the range of our experiment. The anion consists of two $^2\Pi_g$ states separated by a spin-orbit splitting of 410(90) cm^{-1} [23]. The electron affinity (EA), defined as the energy difference between the lowest state of the anion and the lowest state of the neutral, has been measured to be 1.663 ± 0.040 eV [22], and more recently as 1.670 ± 0.015 eV [23]. The neutral ground-state vibrational frequency has been measured to be approximately $\omega'_e = 725\,\mathrm{cm}^{-1}$ with equilibrium bond length $r_e = 1.889$ Å. The anion ground state's vibrational frequency has been measured to be $\omega''_e = 570\,\mathrm{cm}^{-1}$ with an equilibrium bond length of 2.005 Å [22,23]. We treat the overall detachment process primarily as a transition between two harmonic oscillator states; we assume that the Franck-Condon factors for transitions out of a given vibrational level are the same for the two spin-orbit states of the anion.

In addition to the quantized vibrational transitions, in principle the detachment process includes rotational transitions as well as Zeeman and cyclotron structure brought about by the magnetic field of the ion trap. The photodetachment threshold energies are found from a sum of all these contributions:

$$\begin{aligned} E_{th} = ET &+ [(v'\omega'_e) - (v''\omega''_e)] \\ &+ [B'J'(J'+1) - B''J''(J''+1)] \\ &+ \left[\left(n+\tfrac{1}{2}\right)\hbar\omega_c\right] \\ &+ \mu_m H(g'm' + g_e m_e - g''m''), \end{aligned} \tag{1}$$

where the single primes denote the initial state and the double primes denote the final state. The first term on the right-hand side, ET, gives the energy of the overall electronic transition. The second term gives the vibrational contribution described previously and determined by the vibrational quanta v' and v''. The third term gives the rotational transition energy determined by the rotational quanta J' and J''. The rotational constants are given by

$$B = \frac{h^2}{8\pi^2 \mu r_e^2}, \tag{2}$$

where μ is the reduced mass of the molecular rotor, which gives rotational constants on the order of 0.25 cm^{-1}. Thus, spacing between rotational thresholds will be given by $2B(J+1)$, where J is the rotational quantum. Small values of J will give rotational level spacings on the order of 1 cm^{-1}. The highest resolution spectroscopy conducted in this work has a point spacing on the order of 10 cm^{-1}; thus, any structure in the detachment cross section due to rotational levels should not be discernible. If J is large, we anticipate spectral confusion of a large number of possible transitions.

Likewise, the cyclotron and Zeeman structure observed in previous single-atom detachment studies is not expected to be observable [2,12–14,28]. The fourth term in Eq. (1) gives the cyclotron energy of the outgoing electron, determined by the cyclotron quantum number n and the cyclotron frequency ω_c. The spacing between cyclotron levels in the ion trap field of 1.8 T is on the order of 1 cm^{-1} and is therefore too small to be resolved by the methods of this work. The last term gives the Zeeman transition energy, which in this case is dominated by the electronic angular momentum [29]. The Landé g factors g' and g'' are less than 1 and the magnetic quantum numbers for the electronic states are of order 1. The magnetic moment μ_m is determined by the electronic motion and is at most 2 Bohr magnetons [29]. Thus, for the magnetic field and energy resolution used in this work, the Zeeman transition energies are expected to be of order 1 cm^{-1} and therefore also not resolvable.

Our experiment does not resolve structure due to the magnetic field or due to the molecular rotation; furthermore, the photoelectron's motion is unconstrained along the magnetic field axis. Thus, we model the process as detachment into a photoelectron energy continuum where the energy of the outgoing electron is determined by the photon energy and the molecular vibrational transition. We specifically assume that this transition is between a single vibrational state of a single initial electronic state of the anion and a single vibrational and electronic state of the neutral molecule. Thus, the vibronic detachment threshold energies simplify to

$$E_{th} = ET + v'\omega'_e - v''\omega''_e. \tag{3}$$

Given that these vibrational transitions occur between different electronic states, there are no vibrational selection rules [30]. However, each vibrational transition has a propensity given by the relative Franck-Condon factor, which we calculate using the SPECVIEW shareware [31].

Numerous past experiments investigating detachment from single-atom negative ions have demonstrated the validity of the Wigner law [32], which gives the cross section for photodetachment near threshold as

$$\sigma \propto E(E - E_{th})^{l+\frac{1}{2}}, \tag{4}$$

where l is the orbital angular momentum of the outgoing electron, E is the photon energy, and E_{th} is the threshold energy. Several experiments have exploited the sharp increase in cross section at threshold for s-wave detachment to produce high-precision measurements of threshold energies [1,2,13,14,16,21]. In contrast, the gerade nature of the $^2\Pi$ molecular orbital of the $S_2{}^-$ anion in the current experiment yields only higher-order electron wave functions, analogous to those produced by p-wave and d-wave photodetachment. Thus, the partial cross section σ_p for detachment above a given detachment threshold E_{th} is assumed to vary with the photon energy E as derived by Geltman for homonuclear diatomic anions [25,33]:

$$\sigma_p \propto E(E - E_{th})^{\frac{3}{2}}[1 + B_1(E - E_{th}) + B_2(E - E_{th})^2 + \ldots], \tag{5}$$

where B_1 and B_2 are adjustable constants and E_{th} is given by Eq. (3). The first term will dominate for photon energies close to threshold, and the higher order terms may contribute at higher energies. Below and at a given transition threshold, the partial cross section for that transition is zero. Just above each detachment threshold a new channel opens and we expect the overall, total detachment cross section to increase. However, the gradual increase in cross section for these higher-order electron wave functions means that threshold energies are relatively difficult to measure for diatomic molecules such as O_2 and S_2. Nevertheless, the Geltman theory has been used successfully to model detachment data from the $O_2{}^-$ anion over an energy range exceeding 1.5 eV [33]. Given that our experiment covers an energy range of less than 0.25 eV, we are confident of the validity of the Geltman theory in the present work.

Because the photoelectrons span an energy continuum there is no coherence between the outgoing electron wave functions. Thus the total cross section for photodetachment from the ith initial vibronic state and for a photon energy E is the sum of partial cross sections for all vibrational transitions obeying energy conservation [2]:

$$\sigma_i(E) = \sum_{v'} \mathcal{P}_{\mathrm{FC}}\, \sigma_p, \tag{6}$$

where the sum is taken over all allowed transitions to final vibrational states v' and $\mathcal{P}_{\mathrm{FC}}$ is the relative propensity given by the Franck-Condon factor for the corresponding vibrational transition.

Our experiment does not measure absolute cross sections, but rather measures the percentage of ions surviving laser illumination as a function of photon energy E. By summing over all the initial vibronic states, we use the BIL theory to model this percentage as

$$F(E) = \sum_i f_i e^{-A\sigma_i(E)}, \tag{7}$$

where A is proportional to the total optical flux during the laser illumination period, and f_i is the relative population of the ith initial vibronic state. We calculate the relative populations by assuming the anions populate the initial vibronic states with a Boltzmann distribution determined by the depth of the potential well of the ion trap [26]. Our numerical model also accounts for Doppler broadening effects and includes measured values of the ground-state spin-orbit splitting, the electron affinity, and the vibrational spacing of the anion and the neutral molecule [22,23]. Overall, our model is thus a hybrid of the Geltman theory for photodetachment from homonuclear diatomic molecules [25] and the BIL model for detachment from negative ions in the potential well of an ion trap [1,2].

III. EXPERIMENTAL TECHNIQUE

In this experiment we measure the depletion by photodetachment of $S_2{}^-$ ions over a total range of roughly 2000 cm^{-1} near the electron affinity. The ions are created and stored in a Penning ion trap using a magnetic field of 1.8 Tesla, and illuminated by a broadly tunable Ti:sapphire laser. The technique used here is similar to that in several previous experiments [1,2,10,12–14,16,19].

The anions are created in the trap by a two-step dissociative attachment process to a carrier gas of OCS [24]. The ion creation proceeds as a sequence of two collisions:

$$\begin{aligned} \mathrm{OCS} + e^- &\to S^- + \mathrm{CO}, \\ \mathrm{S}^- + \mathrm{OCS} &\to S_2^- + \mathrm{CO}, \end{aligned} \tag{8}$$

where the initial incident electron comes from a biased, thoriated tungsten filament located just outside the trap region. We find that this ion creation process is highly dependent on the filament bias and therefore on the incident electron kinetic energy, consistent with the results of Ref. [24]. We also find that the ion generation process is strongly dependent on the pressure of the OCS gas in the trap chamber, requiring a pressure of roughly 6×10^{-8} Torr, twice that of many of our previous experiments involving simple creation of S^- [13]. We estimate the number of trapped ions to be on the order of 10^4–10^5 [1,2]. The background pressure of the trap vacuum system is less than 10^{-10} Torr. We confirm the mass of the molecular species in the ion trap with an ion cyclotron resonance. This technique applies the cyclotron frequency to the trap end caps to preferentially drive the anions from the trap, resulting in a mass resonance with a Q factor of approximately 42. After the ions are created in the trap, they remain stored in a harmonic potential well of 7 eV for the duration of the experiment. The appropriate well depth is determined by the mass of the anion, the resonant frequency of oscillation of the ion cloud in the trap, and the axial dimension of the trap. The potential well traps the ions along the axis of the magnetic field ($\hat{z}$), while trapping in the perpendicular plane ($\hat{x}$ and $\hat{y}$) is achieved through the ions' cyclotron motion [2].

We measure the relative number of $S_2{}^-$ anions stored in the trap by driving the ion cloud in a resonant axial motion with a radio frequency voltage on the trap end caps. The resulting image current generated in the trap ring electrode is detected by a tuned *LC* circuit and amplified by a commercial high-frequency lock-in amplifier. The resonant axial driving technique permits us to selectively drive the $S_2{}^-$ ions and ignore any residual S^- ions [1,2].

In some experiments we evaporatively cool the ions in the trap prior to any measurements. This is achieved through an exponential reduction in the dc trapping voltage placed on the trap end caps, diminishing the depth of the harmonic potential well in which the ions are stored. If this well depth reduction is made sufficiently gradual, the hottest ions escape with a disproportionate share of the ensemble's thermal energy. The overall effect is to condense the vibrational energy distribution of the initial states, shifting the Boltzmann distribution toward lower vibrational levels, but with a minimal reduction in the anion sample size. The spectroscopic result of the evaporative cooling is that fewer vibrational transitions are energetically available at any given photon energy.

The ions are illuminated by a tunable Ti:sapphire ring laser pumped by a 5.5-W diode-pumped solid-state laser, as shown in Fig. 2. The laser system produces several hundred milliwatts tuned near the electron affinity of the anion; the wavelength is measured by a commercial wavelength meter to a precision of about 600 MHz. The laser's bandwidth is measured by a Fabry-Perot spectrum analyzer to be approximately 10 GHz, which prevents us from conducting the higher-precision spectroscopy of some of our previous experiments [9–14]. The optical flux through the trap is measured by a photodiode and produces a feedback signal to an optical shutter. This feedback mechanism maintains a constant integrated light fluence through the ion trap throughout repeated cycles of the experiment.

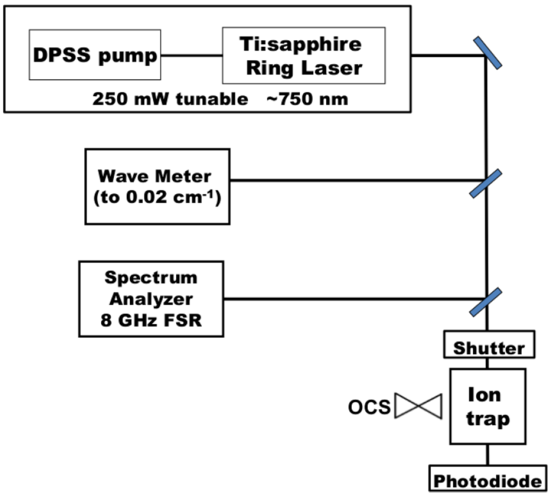

FIG. 2. Schematic diagram of the major optical apparatus and the ion trap. The anions undergo photodetachment with light from a tunable Ti:sapphire ring laser. A photodiode measures the optical power through the trap and provides feedback to a computer-controlled mechanical shutter to maintain a constant total optical fluence from cycle to cycle of the data acquisition.

The photodetachment is recorded by making a relative measurement of the number of anions stored in the trap before and after a laser interaction period of roughly 800 ms. The complete experiment cycle consists of a background noise measurement, an ion creation period of roughly 8 s, the evaporative cooling, the initial ion trap population measurement, the laser illumination period, and the final trap population measurement. There is always some finite loss of ions from the trap due to collisions with the background OCS molecules. We correct for these background losses, to first order, by alternate data acquisition cycles in which we measure the trap retention ratio with no laser interaction. We then fit the vibrational harmonic oscillator model to the measured fraction of ions surviving using the adjustable parameters.

IV. RESULTS AND DISCUSSION

In this experiment we collected multiple sets of laser photodetachment spectroscopy data to measure the fraction of $S_2{}^-$ anions surviving laser illumination as a function of photon energy. These experiments were conducted over a range of energies both above and below published values of the electron affinity of 13 469 (120) cm^{-1} and 13 413 (320) cm^{-1} [22,23]. Our measurements were made at magnetic fields of 1.8 Tesla in the Penning ion trap described above. Preliminary spectroscopy showed a significant decrease in the percentage of ions surviving detachment in the range of the previously measured values of the electron affinity. In an effort to detect periodic vibrational structure, a broad scan over roughly 2000 cm^{-1} was conducted. Figure 3 shows the percentage of anions surviving photodetachment as a function of photon energy, with a nearly linear overall trend of increasing detachment with increasing photon energy. The approximate location of the electron affinity near 13 450 cm^{-1} is indicated by the arrow. A significant amount of detachment occurs at photon energies below the electron affinity, confirming that the

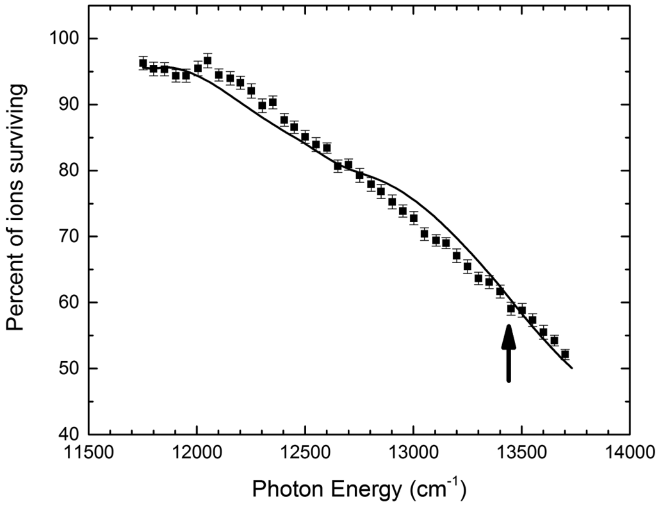

FIG. 3. Broad, low-resolution scan of photodetachment above and below the expected electron affinity, indicated approximately by the arrow. The solid line is a fit of the model to the data. The arrow indicates the approximate location of the expected electron affinity near 13 450 cm^{-1}.

S_2^- anion cloud has enough thermal energy to occupy several excited vibrational states. In fact, the range of detachment below the electron affinity is consistent with the ion trap well depth and an empirical rule of thumb regarding average particle energy [26]. According to this rule of thumb, we should expect the average thermal energy of the trapped anions to be approximately 10% of the trap well depth. Given the trap depth of 7 eV, we expect the average anion thermal energy to be roughly 5650 cm^{-1}. For a diatomic anion with seven quadratic degrees of freedom, we expect roughly 1600 cm^{-1} on average in vibrational energy, which is very closely the range of detachment we observe below threshold. This result strongly corroborates the average particle energy rule of thumb. With an expected vibrational spacing of 570 cm^{-1} in the ground state of the anion, we conclude that a significant population of the anions begins in the first four vibrational levels ($v'' = 0$ to $v'' = 3$).

The hybrid model shown in Eq. (7) is fit to the data (shown by the solid line in Fig. 3) using adjustable parameters, including an overall offset and coefficient, the photon fluence, the anion temperature, and the Geltman coefficients found in Eq. (5). These parameters are adjusted to demonstrate a compatibility of the model to the overall pattern of the data. All other factors—including the Franck-Condon factors, the spin-orbit splitting, the electron affinity, and the vibrational spacings of the anion and the neutral—are held constant. The numerical model accounts for 12 initial vibronic states (the six lowest initial vibrational states in each of the two electronic ground states) and six final vibrational states of the ${}^3\Sigma_g^-$ neutral anion. For each photon energy the total cross section for each initial vibronic state is calculated from the Geltman theory [Eq. (5)] by summing the partial cross sections for each energetically allowed transition weighted by the appropriate Franck-Condon factors [Eq. (6)]. The relative population of each initial state f_i is determined by the Boltzmann factors weighted by the partition function. The model in Fig. 3 is shown for an anion temperature of 2300 K, which is approximately the temperature expected for the well depth of 7 eV. While the details of these data and the model indicate some nonlinearities in the fraction of ions surviving detachment, in general both the data and the model show a steady decrease in the fraction of ions surviving detachment as the photon energy increases. We attribute the generally smooth pattern in both the data and the model to the fact that numerous overlapping vibrational transitions occur with varying Franck-Condon factors from a thermal distribution of initial states.

To examine the possible effects of evaporative cooling on the detachment spectroscopy, the broad scan shown in Fig. 3 was repeated with two different levels of cooling. In each case the anion population was cooled by reducing the well depth from 7.00 eV using the method described in Sec. III. Figure 4 shows the results for the well depth reduced to 6.00 eV and 5.25 eV, and the noncooled results from Fig. 3 repeated for comparison. Again we show the percentage of anions surviving laser illumination as a function of photon energy. We expect the evaporative cooling to condense the thermal distribution of initial states to the lower vibrational states, reducing the amount of detachment observed for photon energies below the electron affinity. The model curves shown in Fig. 4 are calculated for 2300 K, 1970 K, and 1725 K (the expected anion temperatures for the respective well depths of 7.00 eV, 6.00 eV, and 5.25 eV used in the experiment), keeping the other parameters fixed. The data clearly show the evaporative cooling effect, illustrating that the reduction in detachment correlates strongly with the level of cooling. These results confirm the expectation that a large fraction of the uncooled ions occupies several excited initial states, and that transitions from these states contribute to the detachment at photon energies below the electron affinity. The data also show a notable decrease in detachment for photon energies above the electron affinity. However, we note that the Franck-Condon factors are dramatically lower for transitions from the lower initial vibrational states. For example, the Franck-Condon factors for transitions from $v'' = 0$ are roughly five orders of magnitude smaller than for corresponding transitions from $v'' = 3$. Thus, as the anions are evaporatively cooled and condense into lower initial vibrational states, detachment becomes significantly less probable. The overall effect is a reduction in detachment, or an increase in percentage of ions surviving laser illumination, for photon energies both below and above the electron affinity over a range of approximately 2000 cm^{-1}. Overall, the data show that with evaporative cooling we can redistribute a thermal population of initial states in the Penning ion trap. This ability may prove useful in future experiments in which we would like to diminish the motional Stark effect that limits spectroscopic resolution.

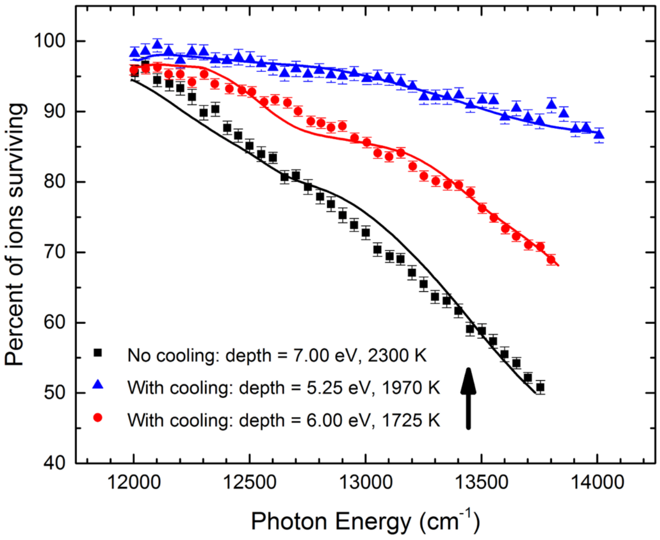

FIG. 4. Photodetachment spectroscopy of S_2^- with evaporative cooling to two different thermal energies. The results of Fig. 3 (without cooling) are also shown for comparison. The solid lines show the model for temperatures of 2300 K, 1970 K, and 1725 K for the respective trap well depths. The arrow indicates the approximate location of the expected electron affinity.

The small drop in anion survival that appears in the data at approximately 13 450 cm^{-1} is very near the expected value of the electron affinity, and was observed in several repetitions of the experiment. Such a decrease in anion survival corresponds to an increase in photodetachment cross section for one or more initial vibronic states, as given in Eq. (7). We don't *a priori* expect a sudden dip in the detachment ratio; in fact, the Geltman model given in Eq. (5) shows that the partial cross sections should rise gradually above each transition threshold (including that of the electron affinity). We note, however, that this experiment does not measure cross section, but rather measures the ratio of ions surviving photodetachment. Equations (6) and (7) show us that this ratio is a sum of exponential decays whose terms depend on each initial state's total cross section and a Boltzmann distribution. In turn, each total cross section is a sum of numerous partial cross sections from overlapping transitions, each with widely varying Franck-Condon factors. We also note that the nonlinearity near the electron affinity appears to be more pronounced for the case in which the ions were cooled to the well depth of 6 eV. This is also consistent with evaporative cooling that effectively shifts anion population to the lower vibrational levels. With higher population in the $v'' = 0$ level, the increase in detachment occurring just above the electron affinity should be larger, as compared to the data for the noncooled anions. The hybrid model does not reflect any notable structure at the electron affinity, so we conclude that the model may be incomplete. Further tests will be necessary to more fully evaluate the model, such as spectroscopy with resolution higher than is currently feasible, as well as spectroscopy on other cooled anion species.

V. CONCLUSIONS

Photodetachment spectroscopy of the $S_2{}^-$ anion both above and below the expected electron affinity has been conducted in a Penning ion trap, with and without evaporative cooling of the trapped anion population. A hybrid model of the experiment is developed from two theories: (1) that of Geltman [25] to calculate the photon energy dependence of the cross section and (2) that of Blumberg, Itano, and Larson [2] to calculate the fraction of ions surviving laser illumination as a function of photon energy. Both the hybrid model and the data show a generally smooth, gradual increase in detachment as a function of photon energy. We attribute this smooth shape to several factors: the multitude of overlapping vibrational transitions and their widely varying Franck-Condon factors as well as the gradual increase in partial cross sections above threshold as stated in the Geltman theory. The overall energy range of photodetachment below the electron affinity is consistent with the ion trap well depth and the expected average thermal energy of the trapped anion population. Evaporative cooling of the anion sample allows us to condense the anions into the lower vibrational states, greatly diminishing the amount of detachment for photon energies below the electron affinity. While lacking notable structure, the hybrid model reflects the general pattern of the anion survival rate by taking into account the expected anion average thermal energy. This result corroborates the rule of thumb described in Ref. [26] regarding average thermal energy of trapped ions.

The hybrid model developed and the techniques used in this work will be used in several future experiments. It is expected that vibrational structure in the photodetachment spectroscopy might be made more apparent by increasing the overall photon fluence. Modifications and adjustments to the laser and optical apparatus will make this feasible. Likewise, a reduced laser bandwidth will make higher resolution measurements possible. Greater contrast in vibrational structure will improve our ability to measure vibrational spacing and perhaps the electron affinity. Comparison of such results with the current work may yield insight into the degree of validity of the hybrid model. Furthermore, adjustments to the rate of evaporative cooling determined by the exponential decay constant may allow us to optimize the efficacy of the cooling. Improvements in the evaporative cooling will permit enhanced spectroscopy overall by diminishing the motional Stark effect [10]. We also anticipate using these same techniques to probe photodetachment from several other ions that can be prepared and trapped, such as SD^- and OD^-.

ACKNOWLEDGMENTS

Acknowledgment is made to Davidson College as well as the donors of the American Chemical Society Petroleum Research Fund for partial support of this research.

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