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Single-photon spectroscopy of singlet sulfur atoms and the autoionization lifetime measurements of the superexcited singlet states

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Single-photon excitation spectra from the lowest singlet ${}^{1}D_{2}$ level of sulfur atoms were recorded with a tunable vacuum ultraviolet (VUV) radiation source generated by frequency tripling in noble gases. The photolysis of CS₂ at 193 nm was used to produce the singlet $S(^{1}D_{2})$ sulfur atoms that were then excited to neutral superexcited states with the tunable VUV radiation. These superexcited states undergo autoionization into the first ionization continuum state of $S^+({}^4S^o_{3/2}) + e^-$, which is not directly accessible from the $S(^{1}D_{2})$ state via an allowed transition. The excitation spectra were recorded by monitoring the S^+ signal in a velocity imaging apparatus while scanning the VUV excitation wavelength. Three new lines were observed in the spectra which have not been previously reported. The full widths at half maximum (FWHM) of each of the observed transitions were determined by fitting the profiles of each absorption resonances with the Fano formula. Autoionization lifetimes τ of these singlet superexcited states were obtained from FWHM using the Uncertainty Principle. Abnormal autoionization lifetimes were found for the $3s^23p^3(^2D^\circ)nd(^1D_2)$ and the $3s^2 3p^3(^2D^0)ns(^1D_2)$ Rydberg series, in which $\tau(5d)$ and $\tau(7s)$ are shorter than $\tau(4d)$ and $\tau(6s)$, respectively. This is contrary to the well-known scaling law of $\tau(n^*) \propto n^{*3}$, which should be followed within a series unless there exist perturbations from other series or new channels open up to which some members of the series can decay. Possible perturbations from the nearby triplet series are suspected for causing the broadening of the 5d and 7s levels. © 2005 American Institute of *Physics*. [DOI: 10.1063/1.1875032]

I. INTRODUCTION

Spectroscopic measurements indicate that sulfur and oxygen ions dominate the torus plasma of the Jupiter satellite Io.^{1,2} In the Sun, sulfur is one of the more abundant elements.³ Thus the study of the photoabsorption and photoionization of sulfur is of great astrophysical interest. Sulfur is also interesting because the ground state is an open shell and it is a heavy atom where spin-orbit coupling is large and correlation effects can determine the properties of the excited state. The electronic configuration of atomic sulfur is $1s^22s^22p^63s^23p^4$, which gives rise to the following electronic states ${}^{3}P_{2,1,0}$, ${}^{1}D_{2}$, ${}^{1}S_{0}$, where the ${}^{3}P_{2}$ is the ground electronic state. The photoabsorption and photoionization spectra of atomic sulfur have been extensively studied in the past.⁴⁻⁶ Tondello reported the absorption spectrum and the absolute cross section of sulfur in the energy region from the ionization threshold at 119.67 nm to 90 nm using the flash pyrolysis method.⁴ More detailed analysis in the region between 100 nm and 109 nm was carried out by Joshi et al.⁵ More recently, Berkowitz et al. measured the photoionization spectrum of sulfur in the region between the first ionization threshold and 92.5 nm.⁶ They assigned many of the lines to the Rydberg series which converge on the ${}^{4}S^{0}$, ${}^{2}D^{0}$, ${}^{2}P^{0}$ states of the S⁺ ion that originate from the ground state of sulfur. They also showed that the autoionization features of the $3p^{3}(^{2}D^{0})nd^{3}D^{0}$ levels are broad while those of the

 $3p^{3}(^{2}D^{\circ})nd \ ^{3}S^{\circ}, \ ^{3}P^{\circ}$ levels are narrow. These studies focused on the triplet states and few experiments have been reported on the singlet states. This is especially true for studies that determine the lifetimes of the singlet states of sulfur. Joshi and co-workers assigned two singlet Rydberg series $3s^23p^3(^2P)ns {}^1P_1$ and $3s^23p^3(^2P)nd {}^1D_2$ that start from the singlet $3s^23p^{4-1}D_2$ state and converge on the ${}^2P^{0}$ ionic state. Using two-photon spectroscopy Pratt observed and assigned several new Rydberg series arising from two configurations of $({}^{2}D^{0})np$ and $({}^{2}D^{0})nf$, which have been excited via twophoton transitions from the singlet $3s^23p^4 {}^1D_2$ state.⁷ He measured linewidths of 2.0-2.5 cm⁻¹ for these two-photon transitions, and concluded that the linewidths in the sulfur spectra were resolution limited, rather than lifetime broadened. No data have been reported for the autoionization rates for the singlet levels of sulfur, except a recent report on the level $3s^2 3p^4 (^2D^\circ) 4d (^1D_2)$ at 11.317 eV.⁸ The observation of fluorescence suggested that the autoionization rate constant for the $(^{2}D^{0})4d^{-3}P^{0}$ levels must be of the order of 10^{9} s⁻¹ or smaller.⁹ The slow autoionization rates of the $3s^23p^3(^2D^{\circ})nd^3P^{\circ}$ levels can be understood on the basis of parity change upon ionization to the $3s^23p^3S^+(^4S^0) + e^-$ continuum within LS coupling. In order to build a ${}^{3}P$ level from this continuum, the free electron needs to be a p electron with angular momentum of l=1, which thus results in even parity rather than the odd parity of the autoionizing $3s^2 3p^3 (^2D^{\circ}) nd {}^3P^{\circ}$ levels. As discussed previously,^{6,7} within the LS coupling approximation, direct ionization of the singlet states between the two lowest ionization thresholds is

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FIG. 1. Single-photon spectroscopy of the singlet atomic sulfur $S(^{1}D)$ at different pressures of the four-wave mixing gas. The Rydberg assignments are based on the data listed in the NIST Atomic Database (Ref. 17). Peaks with question marks have not been previously reported. In section (a) the VUV light is produced by frequency tripling in Kr; in section (b) the VUV light is produced by frequency tripling in Xe. The scan rate of the dye laser was 0.004 nm/s.

forbidden to the $S^+({}^4S^\circ) + e^-$ continuum by the spin selection rule. These singlet states can only autoionize through spin-orbit and/or spin-spin interactions that lead to the breakdown of the *LS* coupling and the autoionization rate is expected to be slow.

Fewer studies have been done on the singlet states compared to the triplet states of the atom because of the difficulty of preparing enough singlet state sulfur atoms in a molecular beam. It will be shown that this limitation can be overcome by using laser photolysis of a proper precursor to produce enough singlet state atoms in a pulsed molecular beam. Strong signals can be obtained for the autoionizing states because the photolysis and ionization lasers cross the molecular beam at the same place and at about the same time when the atom density is at a maximum. This coupled with the high collection efficiency of the ion velocity imaging system provides an excellent signal to noise ratio for these studies.

The photodissociation dynamics of CS₂ at 193 nm have been extensively studied^{10–15} and it is well known that the photolysis of CS₂ gives rise to sulfur atoms in both the ground (³*P*) and excited (¹*D*₂) states. In this paper, a tunable VUV radiation source is used to study the single-photon excitation spectroscopy of the lowest ¹*D*₂ level of sulfur atoms, and to determine the autoionization lifetimes of several excited singlet states between the two lowest ionization thresholds of S⁺(⁴S^o_{3/2}) and S⁺(²*D*^o_{3/2}).

II. EXPERIMENT

The ion velocity imaging apparatus that has been previously described in detail¹⁶ was used for the present measurements. It consists of three stainless steel chambers all pumped with separate turbo-molecular pumps. The first chamber is the molecular beam source chamber, which houses a piezoelectric pulsed valve with a nozzle having a diameter of 0.25 mm. The molecular beam is skimmed twice before it interacts with the laser beams. The second chamber is the reaction chamber where the molecular beam crosses the laser beams. During the experiments the typical pressure in this chamber is 4×10^{-5} Pa. The counter-propagating laser beams enter the reaction chamber in a direction that is perpendicular to the molecular beam and intercept the molecular beam in the center of the ion optics of the time of flight mass spectrometer (TOF-MS). The ion optics of the TOF-MS consist of three plates, a repeller, an accelerator, and a ground plate, the last of which is the entrance to the flight tube for the mass spectrometer. High voltages with the appropriate ratio for ion velocity imaging are applied to the repeller and accelerator plates to focus the ions at the microchannel plate detector. The typical voltages used in the present experiments are 1500 V and 1042 V for the repeller and accelerator, respectively. In order to avoid any effects of electric field on the linewidth measurement, the voltages on the ion optics are applied 300 ns after the arrival of the ionization laser in the interaction region. The pressure in the flight tube during an experiment is about 8×10^{-7} Pa. This is low enough so that the ion cloud can fly for 62 cm without a collision in the field-free flight tube before it strikes the detector. The detector assembly consists of two microchannel plates and a fast P47 phosphor screen. A charge-coupled device camera and a photomultiplier tube are mounted behind the screen to collect images and record the TOF spectra, respectively. The gate from a Boxcar Integrator (SR250) was set on top of the S^+ ion peak in the TOF spectra, and the integrated signal was recorded as a function of the VUV wavelength.

The CS₂ molecular beam is crossed with an unfocused 193 nm laser beam produced by a GAM laser (EX5), and the $S({}^{1}D_{2})$ atoms are ionized by a counter-propagating beam of coherent VUV radiation that is obtained by frequency tripling a UV laser. A Scanmate 2 dye laser operating with the Pyridine 2 dye is pumped by the 532 nm output of a

Nd-YAG (YAG-yttrium aluminum garnet) laser (Spectra-Physics, Pro-230-30). The wavelength of the dye laser is calibrated with a wavelength meter (COHERENT WaveMasterTM). The dye laser output is frequency doubled in an Inrad autotrack unit which keeps the UV output relatively stable as wavelength of the dye laser is scanned. The UV beam is separated from its fundamental with a prism and is focused with a quartz lens into a gas cell which has a lithium fluoride (LiF) lens as the exit window. The cell was filled with Krypton (Kr) or Xenon (Xe) gases in order to generate VUV light in different wavelength regions. The focal length of the quartz lens is 15 cm and the UV light is focused about 6.5 cm in front of the LiF lens that has a 6.5 cm focal length in the VUV region. This assures that the VUV light is collimated when it crosses the molecular beam while the UV light is diverging.

III. RESULTS

A. Excitation spectra

Photodissociation of CS2 at 193 nm produces sulfur atoms in both $S({}^{3}P)$ and $S({}^{1}D)$ states, and the VUV radiation arrives at the reaction center 20 ns after the 193 nm photolysis laser. A strong S⁺ signal appears in the TOF spectra when the VUV wavelength is tuned in resonance with the transitions between the lowest $S(^{1}D)$ level and the superexcited singlet levels above the first ionization continuum. The S⁺ ions are produced via the autoionization of the superexcited singlet sulfur atoms to the $S^+({}^4S^o_{3/2}) + e^-$ continuum. No S^+ ion signal can be detected when the Kr or Xe gas is evacuated from the VUV gas cell, i.e., in the absence of VUV radiation. The S⁺ ion signal as a function of VUV wavelength is recorded using a Stanford Research Boxcar Averager (SR250). The single photon excitation spectra of the singlet sulfur $S(^{1}D)$ are shown in Fig. 1 in two sections. In section (a), the VUV light in the region from 81950-82350 cm⁻¹ is generated by frequency tripling in Kr, while in section (b) from 84550 to 85050 cm^{-1} by frequency tripling in Xe. The conversion efficiency for generating VUV from UV varies at different gas pressures. The spectra shown in Fig. 1 at different pressures indicate that they are reproducible and the widths of the peaks are not due to power broadening. The relative intensity of the VUV light within a section should be comparable, but it is not comparable between the two sections because the efficiencies for VUV conversion in Xe or Kr are different from each other. It should also be noted that in section (b) there is a direct ionization continuum background underlying the resonance peaks because the photon energy in this region is high enough to ionize $S({}^{3}P)$ state atoms. However, the ionization cross section for $S({}^{3}P)$ state seems to be flat in this energy region just above the first ionization continuum, so the direct ionization of $S({}^{3}P)$ is not expected to affect the measured linewidths.^{5,6} The residual UV radiation from the frequency tripling process has no effect on the linewidths on the spectra in section (a), although the total energy of VUV+UV is much higher than the ionization continuum for the singlet states. So we do not expect that the broader linewidths in section (b) are caused by further excitation of the levels by the UV photons.



FIG. 2. The fits to the Rydberg lines. (a) $(^{2}D^{o})4d^{-1}D_{2}^{0}$ level at an excitation energy of 82 037 cm⁻¹; (b) $(^{2}D^{o})6s^{1}D_{2}^{0}$ level at an excitation energy of 82 306 cm⁻¹; (c) $(^{2}D^{o})5d^{1}D_{2}^{0}$ at an excitation energy of 84 630 cm⁻¹. The energy of each of the Rydberg levels equals the sum of the excitation photon energy and the energy of the S (^{1}D) state which is 9 238.6 cm⁻¹ above the ground S $(^{3}P_{2})$ level.

The assignments in Fig. 1 are made according to the energy levels listed in the NIST Atomic Spectra Database.¹⁷ The peaks with question marks in section (b) are not in the NIST database and have been observed here for the first time. Their possible assignments will be discussed below. These peaks are at photon energies of 84778 ± 1 , 84811 ± 1 , and 84888 ± 1 cm⁻¹. The uncertainty in the energy should be within 1 cm⁻¹ considering the bandwidth (~0.6 cm⁻¹) of the VUV light and other systematic errors.

The slowest scan rate available on the dye laser (0.001 nm/s) was used to record each of the lines shown in Fig. 1 so that a more precise linewidth for each transition line could be determined. The resulting spectra at this scan rate are shown in Figs. 2–4. Assuming that the dye laser has a Gaussian line shape, then the line shape of the VUV radiation obtained by frequency tripling will also be approximated by a Gaussian shape. The bandwidth in the VUV should be at most 0.6 cm⁻¹ because the fundamental of the dye laser has a bandwidth of 0.09 cm^{-1} in this wavelength region. Convolution of a Fano profile^{18,19} and a Gaussian function for the laser bandwidth of 0.6 cm^{-1} has been used to fit the experimental profiles. As shown in the figures, the fits are very good. The full width at half maximum (FWHM) is determined from the deconvoluted Fano profile of each line, and the corresponding autoionization lifetime is calculated



FIG. 3. The fits to the Rydberg lines in the excitation energy region between $84760-84816 \text{ cm}^{-1}$. The energy of each of the corresponding Rydberg levels is the excitation energy plus the energy of the S(¹D) state which is 9 238.6 cm⁻¹ above the ground S(³P₂) level.

using the uncertainty principle, i.e., $\Delta E \tau = h/2\pi$. The FWHM of each line and the corresponding lifetime are reported in Table I. The autoionization lifetime varies from hundreds of femtoseconds to a few picoseconds.

B. Possible assignments of the new peaks

The three new peaks observed in the photoionization spectrum are at photon excitation energies of 84778 ± 1 , 84811 ± 1 , and 84888 ± 1 cm⁻¹. At these energies and all other energies shown in Fig. 1(b), the S(³P) can be ionized since the energies are higher than the first ionization energy

of 10.36 eV.¹⁷ However, as shown in Fig. 5, all images taken on the peaks are identical and originate mostly from the excitation of the $S(^{1}D)$ atoms, as has recently been reported.⁸ The image taken at about 84 690 cm⁻¹ arises from the ionization of the sulfur atoms produced in the $S(^{3}P)$ state. The absolute energies for all the levels (shown as peaks) in Fig. 1 equal the sum of the excitation photon energy and the energy of the $S(^{1}D)$ level of 9 238.6 cm⁻¹.¹⁷

Quantum defects μ are calculated using the relationship $\mu = n - n^*$, where n^* is the effective principal quantum number defined by



FIG. 4. The fit to the Rydberg line in the excitation energy region of $84\,820-84\,940$ cm⁻¹. The energy of the corresponding Rydberg level is the excitation energy plus the energy of $S(^{1}D)$ which is 9 238.6 cm⁻¹ above the ground $S(^{3}P_{2})$ level.

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TABLE I. The energies of the autoionization Rydberg lines observed in the spectra along with their FWHM, q parameters, and lifetimes obtained by fitting the profiles with the Fano formula. The uncertainty of the FWHM is about 0.2 cm⁻¹.

Level (cm ⁻¹) ^a	$E_r(\mathrm{cm}^{-1})^{\mathrm{b}}$	FWHM $\Gamma(cm^{-1})$	<i>q</i> parameter	Lifetime (ps)	Transition assignment
91 276	82 037	0.9	>60	5.9	$(^{2}D^{0})4d(^{1}D_{2}^{0})-3s^{2}3p^{4}(^{1}D_{2})$
91 545	82 306	0.7	>60	6.6	$(^{2}D^{o})6s(^{1}D^{o}_{2})-3s^{2}3p^{4}(^{1}D^{o}_{2})$
91 517	82 278	Too weak			$(^{2}D^{0})4d(^{3}P_{2}^{0})-3s^{2}3p^{4}(^{1}D_{2})$
93 869	84 630	4.2	>60	1.3	$(^{2}D^{o})5d(^{1}D^{o}_{2})-3s^{2}3p^{4}(^{1}D^{o}_{2})$
94 035	84 797	7.8	10	0.7	$(^{2}D^{0})7s(^{1}D_{2}^{0})-3s^{2}3p^{4}(^{1}D_{2})$
94 016	84 778	0.8	-8	6.6	(Unknown)- $3s^2 3p^4({}^1D_2)$
94 049	84 811	0.8	-7	6.6	(Unknown)- $3s^2 3p^4({}^1D_2)$
94 127	84 888	14.6	-10	0.4	$(\text{Unknown}) - 3s^2 3p^4 (^1D_2)$

^aAbsolute energies for the observed levels, which equal to the VUV photon energy (second column) plus the energy of the $S(^{1}D)$ 9239 cm⁻¹.

^bVUV excitation photon energy.

$$n^* = \sqrt{R_s/[E(\mathrm{IP}) - E_{nl}]}.$$

Here, R_s is the Rydberg constant for sulfur ($R_s = 109735.44 \text{ cm}^{-1}$), E_{nl} is the energy of Rydberg state, and E(IP) is the ionization potential of the state to which the Rydberg state is converging. In the assignments $(^2D^0)nd/ns$ shown in Fig. 1, the Rydberg states converge on the first excited state of S^+ , 2D . The $S^+(^2D)$ includes two spin-orbit states, the $^2D_{3/2}$ and the $^2D_{5/2}$, but the weighted average of the $^2D_{3/2}^0$ limit (98 412.0 cm⁻¹) and the $^2D_{5/2}^0$ limit (98 443.8 cm⁻¹) was used to calculate the effective principal quantum number n^* as described in Ref. 6. Considering there are two different Rydberg series corresponding to the $^2D_{3/2}^0$ limit and the $^2D_{5/2}^0$ limit as described in j_cl coupling, 7,20,21 the effective principal quantum numbers can then be calculated according to their own limits. The results are shown in Table II. As can be seen, for the $(^2D^0) nd$ series the quantum defects in bold that were calculated with the $^2D_{3/2}^0$ limit in the

second to last column are a closer match than those calculated assuming the ${}^{2}D_{5/2}^{0}$ limit, so it is probably more appropriate to assign $({}^{2}D^{\circ})nd$ series as $({}^{2}D_{3/2}^{\circ})nd$ instead of $({}^{2}D_{5/2}^{\circ})nd$. Similarly, for the $({}^{2}D^{\circ})ns$ series it is probably more appropriate to assign $S^{+}({}^{2}D_{5/2}^{\circ})$ instead of $S^{+}({}^{2}D_{3/2}^{\circ})$ as its limit. Then two of the new peaks at 94 015.6 cm⁻¹ and 94 049.2 cm⁻¹ can be assigned $as3s^{2}p^{3}({}^{2}D_{3/2}^{\circ})7s$ and $3s^{2}p^{3}({}^{2}D_{5/2}^{\circ})5d$, respectively. We have been unable to assign the peak at 94 127.0 cm⁻¹. The present assignments are based on only a few lines and to confirm the assignments a longer spectral scan is required so that more lines in the series can be observed.

IV. DISCUSSION

Although photoabsorption and photoionization spectra of sulfur have been studied extensively and many of the autoionization levels of the sulfur atom have been previously



FIG. 5. The images taken on all the peaks show the characteristic energy and angular distributions of the $S(^{1}D)$ fragments and the image taken on the continuous background at about 84 690 cm⁻¹ shows those of the $S(^{3}P)$ fragments produced by photolysis of CS₂ at 193 nm. (Ref. 29).

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TABLE II. New Rydberg assignments of the autoionization lines, the effective principal quantum numbers n^* , and the quantum defects μ are calculated using the ${}^2D^{o}_{3/2}$ and ${}^2D^{o}_{5/2}$ ionization limits.

		n^*		μ	
Level (cm ⁻¹)	New assignment	$^{2}D_{3/2}^{0}$	${}^{2}D^{0}_{5/2}$	$^{2}D_{3/2}^{0}$	${}^{2}D_{5/2}^{0}$
91 276	$3s^2 3p^3 (^2D^o_{3/2}) 4d$	3.921	3.913	0.079	0.087
91 545	$3s^2 3p^3 (^2D^{o}_{5/2})6s$	3.997	3.988	2.003	2.012
93 869	$3s^2 3p^3 (^2D^o_{3/2})5d$	4.915	4.898	0.085	0.102
94 035	$3s^2 3p^3 (^2D^{o}_{5/2})7s$	5.007	4.989	1.993	2.011
94 016	$3s^2 3p^3 (^2D^{o}_{3/2})7s$	4.996	4.978	2.004	
94 049	$3s^2 3p^3 (^2D^{o}_{5/2})5d$	5.015	4.997		0.003
94 127	?	5.061	5.042		

assigned,⁴⁻⁶ to our knowledge the only report on the autoionization lifetime of the superexcited singlet level is in Ref. 8 for $S(^{2}D^{o})4d^{-1}D_{2}$. There have, however, been a few measurements of the autoionization lifetime for atomic oxygen. The O $({}^{2}D^{0})3p {}^{1}P_{1}$ and ${}^{1}F_{3}$ levels were first observed in the emission studies by Edlen²² and by Eriksson and Isberg.²³ The transitions involving the ${}^{1}P_{1}$ level were broadened by approximately 0.2 cm⁻¹ with an autoionization lifetime of 3×10^{-11} second to the ${}^{4}S_{3/2}^{0}$ continuum. The transitions involving ${}^{1}F_{3}$ level were sharper and hence the lifetimes were longer.²³ Recently, Pratt and co-workers reported the autoionization of $O(^2D^0)3p$ 1P_1 and 1F_3 levels excited from the $O(^{1}D_{2})$ state by two-photon absorption.²⁴ They evaluated the autoionization lifetimes of the ${}^{1}P_{1}$ and ${}^{1}F_{3}$ levels and found that they were longer than 3×10^{-10} s and 5.8×10^{-10} s, respectively. Smith et al. measured the autoionization lifetimes for the $(^{2}D^{0})3p$ $^{1,3}P$ and $(^{2}D^{0})3p$ ^{3}D , ^{3}F states by measuring the Rabi oscillations which were induced when the atoms were excited from the ground ${}^{3}P_{2}$ state by multiphoton process. The autoionization lifetimes are of the order of 10^{-10} s for all the states except the $(^{2}D^{0})3p$ ^{3}P state which has a 6 fs lifetime.²⁵ More recently, single-photon ionization of atomic singlet oxygen $O(^{1}D_{2})$ was investigated by Flesch and co-workers.²⁶ The photoionization efficiency spectrum was recorded between the onset of the first $({}^{2}S^{o})$ and the second $(^{2}D^{0})$ ionization thresholds. But no lifetime measurement was reported.

Gibson et al. reported the photoionization spectrum of sulfur in detail between the first ionization threshold and 92.5 nm. They assigned many of the triplet autoionization states which converge to the ${}^{4}S^{0}$, ${}^{2}D^{0}$, ${}^{2}P^{0}$ states of the S⁺ ion originating from the ground state of Sulfur $({}^{3}P_{2})$.⁶ Of the four series converging to ${}^{2}D^{0}$, they found that three of them, $(^{2}D^{\circ})nd \ ^{3}P^{\circ}$, $(^{2}D^{\circ})ns \ ^{3}D^{\circ}$, $(^{2}D^{\circ})nd \ ^{3}S^{\circ}$, were sharp and one, $(^{2}D^{\circ})nd \ ^{3}D^{\circ}$, was broad. In the two-photon spectroscopy studies of the singlet atomic sulfur by Pratt,⁷ several new autoionizing Rydberg series assigned to the $(^{2}D^{0})np$ and $(^{2}D^{0})nf$ configuration were reported. Very narrow linewidths were expected for those levels because autoionization is forbidden within LS coupling. Within the LS coupling approximation, direct photoionization to a ${}^{4}S^{\circ}$ state is forbidden from the singlet states of the atom between the first and the second ionization threshold [to the $(^{2}D^{o})$] since no singlet continua exist in this region. Thus, the only way these states can be ionized is via autoionization to ${}^{4}S^{0}$ as a result of spin-orbit, spin-spin interactions that couple atomic states with different spins.^{27,28} These states were therefore predicted to have long lifetimes. As discussed above, the order of magnitude for the lifetimes of the ^{1}D states in oxygen atom was found to be approximately of 10^{-10} s. However in the current measurements, the autoionization lifetime varies from hundreds of femtoseconds to a few picoseconds. The much shorter autoionization lifetimes in atomic sulfur indicate that the spin-orbit, spin-spin interactions in sulfur are much stronger than in oxygen. Thus, the autoionization rate constant of atomic sulfur is higher than similar states for singlet atomic oxygen. This can be readily understood in terms of the mass of sulfur atom which is twice that of the oxygen atom so one would expect that spin-orbit interaction is much stronger. Furthermore the spin-spin interaction will also play an important role in the autoionization process. In highly excited states, the state mixing between the states with different spin is expected under the spin-spin interaction. The existence of state mixing between the very rapidly ionizing triplet states and the excited singlet states will promote the autoionizing rate of the singlet states.

The profile of an absorption line in the ionization continuum of atomic spectra can be represented by the Fano formula:^{18,19}

$$\sigma(\varepsilon) = \sigma_a[(q+\varepsilon)^2/(1+\varepsilon^2)] + \sigma_b. \tag{1}$$

Here $\varepsilon = (E - E_r) / \frac{1}{2} \Gamma$ indicates the departure of the incident photon energy *E* from an idealized resonance energy E_r which pertains to a discrete autoionizing level of the atom; Γ is the width of the line; $\sigma(\varepsilon)$ represents the absorption cross section for photons of energy *E*; σ_a and σ_b represent the cross sections corresponding, respectively, to transitions to states of the continuum that do and do not interact with the discrete autoionizing state; and *q* is a numerical index which characterizes the line profile. Following the Fano procedure, we are able to fit those autoionization lines with the appropriate parameters. A comparison of the different parameters obtained from the fits is listed in Table III.

According to Fano, Eq. (22) in Ref. 17,

$$\frac{1}{2}\pi q^2 = |(\Phi|T|i)|^2 / |(\psi_E|T|i)|^2 \Gamma.$$
(2)

Here $\frac{1}{2}\pi q^2$ represents the ratio of the transition probabilities of the initial state to the "modified" autoionizing discrete state Φ and to a bandwidth Γ of unperturbed continuum state

TABLE III. A comparison of the parameters used in the fits of the spectrum in Fig. 1(b). Parameters q, Γ , and σ_a are defined by Eqs. (1)–(3). I is the intensity of the line (a.u.). According to Fano theory, the ratio shown in the last column should be a constant. This is true within experimental error.

$E_r(\mathrm{cm}^{-1})$	q	$\Gamma(cm^{-1})$	$\sigma_a(a.u.)$	<i>I</i> (S ⁺) (a.u.)	$I/[(q^2-1)\Gamma\sigma_a]$
84 888	-10 ± 0.5	14 ± 0.4	0.0061	98	12
84 811	-7 ± 0.5	0.9 ± 0.1	0.0088	5	13
84 797	$10 {\pm} 0.5$	7.8 ± 0.4	0.0026	24	12
84 778	-8 ± 0.5	$0.8 {\pm} 0.1$	0.0017	1.1	13
84 630	>60	4.2 ± 0.4	< 0.0005	102	13

 ψ_E . The greater the ratio is the smaller the transition probability to the continuum states. When the transition probability to the continuum states is negligible, the autoionization through the discrete state has a profile represented by a resonance curve with a half-width $\pi |V_E|^2$ which originates from the Fermi Golden rule. In this case, the profile is symmetric and has Lorentzian shape. V_E is

$$V_E = (\psi_E | H | \varphi), \tag{3}$$

where φ is the discrete autoionizing state, ψ_E is the continuum state.

It is interesting to note that the profiles of the $(^{2}D^{0})4d(^{1}D_{2}^{0})$ at 91 276 cm⁻¹, $(^{2}D^{0})6s(^{1}D_{2}^{0})$ 91 545 cm⁻¹ $(^{2}D^{\circ})5d(^{1}D_{2}^{\circ})$ at 93 869 cm⁻¹ are symmetric. For these lines, the q parameters used to fit the Fano profiles could be any value that is greater than 60. This means the transition probability from S(¹D) to the continuum state S⁺(⁴S^o_{3/2})+ e^{-} is negligible which is not surprising because the transition of $S(^{1}D)$ to the continuum state $S^{+}(^{4}S^{0}_{3/2})$ is supposed to be forbidden in the LS coupling. Actually these profiles could also be fit with Lorentzian functions with the same widths as their Fano fits. However, the profiles at 94 016, 94 035, 94 049, and 94 127 cm⁻¹ are asymmetric, only the Fano formula will fit them well. The q parameters used to fit these profiles are much smaller than those used for the symmetric peaks as shown in Table III, which means the transition probability of $S(^{1}D)$ to the continuum state cannot be neglected. This contribution causes interference with opposite phases on the two sides of the resonance; in particular, the transition probability vanishes on one side of the resonance which leads to an asymmetric Fano profile. The breakdown of LS coupling is obvious here. Although the only continuum state here should be $S^+({}^4S^o_{3/2}) + e^-$, as we can see in Table III, the σ_a are different for different discrete autoionizing states. This suggests that the continuum states corresponding to different discrete state are different because the interactions between the discrete Rydberg states and the continuum could modify the continuum which leads to the different transition probabilities to the continuum.

Table I also shows that big differences exist in the autoionization lifetimes between the $({}^{2}D^{o})4d$ level and the $({}^{2}D^{o})5d$ level, as well as between the $({}^{2}D^{o})6s$ level and the $({}^{2}D^{o})7s$ level. The autoionization rate of the $({}^{2}D^{o})5d$ state is about five times faster than that of the $({}^{2}D^{o})4d$ state, while the autoionization rate of the $({}^{2}D^{o})7s$ state is about 11 times faster than that of the $({}^{2}D^{o})6s$ state. These observations are contrary to the scaling rule that states the linewidths Γ of a given autoionizing series will tend to decrease with increasing effective principal quantum number n^* as $\Gamma \propto 1/(n^*)^3$.^{18,19} Current observations suggest that there exist perturbations in the energy region shown in Fig. 1(b) that give rise to the broadening of the linewidths. The perturbations probably come from the interactions (i.e., mixing) of these singlet states with the nearby triplet states, which have faster autoionizing rate. The energy region shown in Fig. 1(b) corresponds to the wavelength region 1062.2–1065.7 Å of the photoionization spectrum of $S(^{3}P)$ by Gibson *et al.*⁶ In this region there are some broad autoionization peaks arising from the triplet Rydberg states. A level at 94 047 cm⁻¹ was assigned to the $3p^{3}(^{2}D^{0})5d^{3}P^{0}$ level by Gibson *et al.*,⁶ but it was later corrected as $3p^3(^2D^\circ)5d^3F^\circ$ at 94 044 cm⁻¹ by Joshi et al.⁵ According to NIST database¹⁷ the $3p^{3}(^{2}D^{\circ})5d^{3}P^{\circ}$ level should be at 94 414 cm⁻¹. This triplet level of $(^{2}D^{0})5d^{3}F^{0}$ is 5 cm⁻¹ away from the unassigned peak at 94 049 cm⁻¹ and 9 cm⁻¹ away from the $3p^{3}(^{2}D^{0})7s^{1}D_{2}^{0}$ level (94 035 cm⁻¹). Another level at 94 032.6 cm⁻¹ was assigned by Pratt in $j_c l$ coupling scheme as $3p^{3}(^{2}D^{0}_{3/2})5f$ level,⁷ which is 2.4 cm⁻¹ away from the $3p^3(^2D^0)7s^5D_2^0$ level (94 035 cm⁻¹) and could be singlet or triplet state if assigned in LS coupling. However, the nearest level to the $3p^{3}(^{2}D^{0})5d \,^{1}D_{2}^{0}$ level (93 869 cm⁻¹) is the $3p^{3}(^{2}D^{0})7s^{3}D^{0}$ level (93 824 cm⁻¹),⁵ which is 45 cm⁻¹ away. The nearest level to the unassigned level at 94 127 cm⁻¹ (excitation energy at 84 888 cm⁻¹) is the $3p^{3}(^{2}P^{0})3d^{3}D^{0}$ level at 94 180 cm⁻¹.⁶ The weak broad shoulder between excitation energies of 84 820 and 84 860 cm^{-1} (Fig. 4) could be the satellite transition from the $S(^{3}P_{o})$ to the level at 85 433.6 cm⁻¹ assigned by Tondello⁴ as $3p^{3}(^{2}D^{\circ})3d^{3}S^{\circ}$ but by Gibson *et al.* as $3p^{3}(^{2}D^{\circ})5s^{3}D^{\circ}.^{6}$ Unfortunately, no image was taken in this region to verify which sulfur state, ${}^{3}P$ or ${}^{1}D$, was excited. As shown in Fig. 5, there is no doubt that the main peak at 84 888 cm⁻¹ resulted from the excitation of the $S(^{1}D)$ state. As shown above some of the triplet levels are very close to the observed peaks (a few wave numbers away), but some of them are pretty far away (tens of wave numbers away). Or maybe there are some "dark states" that have not been observed. Certainly any interactions between these states will affect the autoionization process. In order to assign the unassigned peaks as well as to better understand the perturbations between the series, a broader spectral range with higher resolution is essential.

The perturbations between the singlet and the short-lived triplet states will likely not only broaden the singlet state linewidth but also change the shape of the absorption line. The apparent asymmetric shapes (small q values) indicate that the interference between the discrete and the continuum states is appreciable. Because the linewidths of the triplet states are very broad and there are many such states in the spectral region of 93840–94 200 cm⁻¹,⁶ in the eyes of the discrete singlet states this region is an effective continuum. If the singlet states have a small triplet character direct excitation to this quasi-continuum will not be negligible. It may not be absolutely necessary to have a direct transition to the true triplet continuum from the S(¹D) state to cause asymmetric line shape.

V. CONCLUSIONS

The single-photon excitation spectra from the singlet ${}^{1}D_{2}$ level of sulfur atoms have been studied using tunable VUV radiation by monitoring the S⁺ signal in a time-of-flight mass spectrometer while scanning the excitation wavelength. Three new levels not previously reported have been observed in the spectra. Fano profiles are used to determine the line profiles for each of the autoionizing resonance transitions. The autoionization lifetimes are calculated from the full widths at half maximum of the line profiles. The autoionization lifetimes for different states vary from a few hundreds of femtoseconds to a few picoseconds which are much shorter than expected based on the fact that there is no singlet ionization continuum in this energy region. The much shorter autoionization lifetimes of superexcited singlet sulfur states indicate that strong spin-orbit, spin-spin interactions exist in this heavy atom. The observed anomalies in lifetimes and absorption line shapes may be attributed to interactions between the singlet levels and the nearby broad triplet levels.

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