Measurement of the autoionization lifetime of the superexcited atomic sulfur S(3s²3p³(²D^o)4d) state using tunable vacuum ultraviolet (VUV) radiation¹

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Abstract: A new method is described that combines a tunable coherent vacuum ultraviolet (VUV) radiation source and an ion velocity imaging apparatus to study the autoionization of superexcited sulfur atoms. The photolysis of CS₂ at 193 nm is used to produce metastable sulfur atoms in the ¹D₂ state. The S(¹D₂) atom is then directly excited to the neutral superexcited state $3s^23p^3(^2D^\circ)4d$ (¹D₂) at 11.317 eV with a tunable VUV photon at ~121.896 nm. This excited state then undergoes autoionization into the first ionization continuum state of S⁺(⁴S_{3/2}) + e⁻, which is not directly accessible from the S(¹D₂) state through optical transition. By monitoring the S⁺ signal in the time-of-flight mass spectrometer while scanning the excitation wavelength, the line profile of the $3s^23p^34d$ ¹D₂ $\leftarrow 3s^23p^4$ ¹D₂ transition is recorded and found to have a full width at half maximum (FWHM) of 0.9 cm⁻¹. This has been used to determine an autoionization lifetime of the neutral superexcited $3s^23p^34d$ ¹D₂ state of 5.9 ps. The accurate measurement of the autoionization lifetime provides a benchmark for testing fundamental theoretical models of processes occurring in excited states of atoms.

Key words: autoionization, atomic sulfur, vacuum ultraviolet (VUV), full width at half maximum (FWHM).

Résumé : On décrit une nouvelle méthode qui combine une source cohérente et réglable de rayonnement ultraviolet du vide avec un appareil d'imagerie de la vitesse des ions pour étudier l'autoionisation d'atomes de soufre surexcités. On a utilisé la photolyse du CS₂ à 193 nm pour produire des atomes de soufre métastables dans l'état ¹D₂. L'atome $S(^{1}D_{2})$ est alors directement excité à l'état surexcité neutre $3s^{2}3p^{3}(^{2}D^{\circ})4d$ ($^{1}D_{2}^{\circ}$), à 11,317 V, à l'aide d'un photon VUV réglable à ~121,896 nm. Cet état excité subit alors une autoionisation dans le premier état d'ionisation continue du $S^{+}(^{4}S_{3/2}^{\circ}) + e^{-}$ qui n'est pas directement accessible à partir de l'état $S(^{1}D_{2})$ par le biais d'une transition optique. En suivant le signal du S⁺ dans un spectromètre de masse à temps d'envol alors qu'on balaye la longueur d'onde d'excitation, on a enregistré le profil de la raie de la transition $3s^{2}3p^{3}4d$ $^{1}D_{2}^{\circ} \leftarrow 3s^{2}3p^{4}$ $^{1}D_{2}$ et on a trouvé que la largeur totale à demi-hauteur maximale (« FWHM ») est de 0,9 cm⁻¹. Cette valeur a été utilisée pour déterminer que le temps de vie de l'autoionisation de l'état surexcité neutre $3s^{2}3p^{3}4d(^{1}D_{2}^{\circ})$ est de 5,9 ps. La mesure précise du temps de vie d'autoionisation fournit une référence pour évaluer les modèles théoriques fondamentaux des processus se produi-sant dans les états excités d'atomes.

Mots clés : autoionisation, soufre atomique, ultraviolet du vide, largeur totale à demi-hauteur maximale.

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Introduction

The study of the photoionization of sulfur is of great interest because of its applications in astrophysics. Spectroscopic measurements indicate that sulfur and oxygen dominate the torus plasma of the Jupiter satellite Io (1, 2). Furthermore, the study of the photoabsorption spectrum of sulfur is interesting because it is an open-shell heavy atom where spin–orbit coupling can be large and correlation ef-

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fects in determining the properties of the excited state can be important. The electronic configuration of atomic sulfur is $1s^2 2s^2 2p^6 3s^2 3p^4$, which gives rise to the ${}^{3}P_{2,1,0}$, ${}^{1}D_2$, and ${}^{1}S_0$ terms. The ground state is the ${}^{3}P_2$ state. The photoionization of ground-state sulfur $({}^{3}P_{2})$ has been extensively studied in the past. The absolute values of the cross sections were reported by Tondello (3) for photon energies from the ionization threshold at 119.67 to 90 nm using the flash pyrolysis method. Sarma and Joshi (4) did the same work but made more detailed analysis in the region between 109 and 100 nm. Berkowitz and co-workers (5) observed the photoionization spectrum of sulfur in the region between the first ionization threshold and 92.5 nm. They assigned many of the autoionization states that converge on the ⁴S^o, ²D^o, ²P^o states of the S⁺ ion originating from the ground state of sulfur $({}^{3}P_{2})$. They also showed that the autoionization features of the $3p^{3}(^{2}D^{o})nd ^{3}D^{o}$ levels are broad, while those of the $3p^{3}(^{2}D^{o})nd \ ^{3}S^{o}, ^{3}P^{o}$ levels are narrow. However, surprisingly, we failed to find previous measurements of the lifetimes

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from these line widths for atomic sulfur. For atomic oxygen, with the similar electronic configuration $1s^22s^22p^4$, Smith and co-workers (6, 7) measured the autoionizing lifetimes originating from the ³P state by a variety of techniques including Rabi oscillation. All of their measurements were based on multiphoton ionization of atomic oxygen (6, 7). Some lifetime measurements of weakly autoionizing states in O I in the region of 75-125 nm were also done by observing the decay rate of emitted photons (8). Fewer studies have been carried out on the superexcited singlet states of oxygen atoms compared to the triplet states, most likely because of the difficulty of producing a high density of atoms in the lower singlet state, from which optical excitation originates. We will show that this limitation can be overcome by using laser photolysis of the proper precursor for the metastable atom in a pulsed molecular beam along with a tunable coherent vacuum ultraviolet (VUV) source to excite the atom to the autoionization state. Strong signals can be obtained for the autoionizing state because the lasers cross the molecular beam at the point in both space and time at which the atom density is at a maximum, as well as because of the high sensitivity of the ion velocity imaging system.

The photodissociation dynamics of CS₂ at 193 nm has been extensively studied (9-14). It is well known that the photolysis of CS₂ gives rise to sulfur atoms in both the ground $({}^{3}P_{2,1,0})$ and excited $({}^{1}D_{2})$ states. The S $({}^{1}D_{2})$ in the beam is then excited using a single VUV photon at 121.896 nm (10.17 eV) to the $3s^2 3p^3 (^2D^{\circ}) 4d {}^1D_2^{\circ}$ neutral state at 11.317 eV, which is above the first ionization threshold of the sulfur atom. This superexcited state then undergoes autoionization into the first ionization continuum of $S^{+}({}^{4}S_{3/2}) + e^{-}$, with its threshold at 10.36 eV. The energy of the photon (10.17 eV) is not high enough to ionize the ground state $S({}^{3}P_{2})$. The relevant energy level diagram of the sulfur atom and ion is shown in Fig. 1. The $3s^23p^3(^2D^o)4d$ ${}^{1}\mathrm{D}_{2}^{0} \leftarrow 3s^{2}3p^{4}{}^{1}\mathrm{D}_{2}$ transition line profile is then recorded by monitoring the S⁺ signal in the time-of-flight mass spectrometer (TOF-MS), while scanning the excitation wavelength.

Experimental

The measurements were performed using an ion velocity imaging apparatus, which has been described in detail elsewhere (15). It consists of three stainless steel chambers that are 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 skimmed molecular beam crosses the laser beams. During the experiments, the typical pressure in this chamber was 4×10^{-5} Pa. The 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 TOF-MS. The ion optics of the TOF-MS consists 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 to focus the ions





into the flight tube that is perpendicular to the plane defined by the laser and the molecular beams. The typical voltage ratio in our experiment was 1500 V/1042 V. To avoid any field effects on the line width measurement, the voltages on the ion optics were applied 300 ns after the arrival of the VUV light in the ionization region. The pressure in the flight tube during an experiment was about 8×10^{-7} Pa. This is low enough so that the ion cloud can fly for 62 cm without a collision in a field-free region before it strikes the detector. The detector assembly consists of two microchannel plates and a fast P47 phosphor screen. A CCD camera and a photomultiplier tube are mounted behind the screen to collect images and TOF spectra, respectively.

The CS₂ molecular beam is crossed with a 193 nm laser beam, which is produced by a GAM laser (EX5). The $S(^{1}D_{2})$ atom is ionized by a coherent VUV radiation beam that is obtained by frequency tripling. A Scanmate 2 (or FL2002) dye laser operating with the Pyridine 2 dye is pumped by the 532 nm output of an Nd:YAG laser (Spectra-Physics, Pro-230-30). The wavelength of the dye laser is calibrated by a wavelength meter (COHERENT WaveMasterTM). The dye laser output is frequency doubled in an Inrad auto-track unit, which keeps the intensity of the UV output the same while the wavelength 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 contains Kr gas that is used for generating the VUV radiation. The focal length of the quartz lens is 15 cm, and the UV light is focused about 6.5 cm in front of a LiF lens with a 6.5 cm focal length at the VUV wavelength so that the VUV light is nearly collimated through the reaction chamber.

Results

Figure 2 shows a series of mass spectra that were obtained under different excitation conditions. A pure CS_2 beam with 50 torr (1 torr = 133.322 Pa) backing pressure was used for

Fig. 2. Time-of-flight mass spectra of CS_2 : (*a*) beam + 193 nm light; (*b*) beam + 121.896 nm light; (*c*) beam + 193 nm light + 121.896 nm light (121.896 nm light arrives 20 ns later relative to 193 nm light).



these experiments. The timing for the pulse valve opening was carefully adjusted so that no clusters were observed in the TOF spectra. Figure 2a shows that CS_2^+ and CS^+ ions are produced by multiphoton ionization even though the 193 nm laser fluence is very low (~1 mJ/cm²) (16). This is because the single and multiphoton absorption cross sections of CS_2 are very large. Figure 2b is the TOF spectrum taken when only the VUV light at 121.896 nm (10.17 eV) was present. The CS₂⁺ signal is the result of single-photon ionization of the CS_2 molecule whose ionization energy is 10.07 eV. Figure 2c shows the TOF mass spectrum when both lasers were present. The 121.896 nm light is delayed 20 ns with respect to the 193 nm laser. A strong S⁺ signal is now seen in the TOF mass spectrum as expected. The S⁺ ion comes from the VUV ionization of the $S(^{1}D_{2})$ atom that is produced by the photodissociation of CS_2 at 193 nm. The S⁺ ion signal disappears when the Kr gas is evacuated from the VUV cell.

The S⁺ ion signal as a function of ionization wavelength was recorded using a Stanford Research Boxcar Averager (SR 250). Figure 3 shows the line profiles obtained when the wavelength of the ionization laser was scanned through the $3s^23p^{3}(^{2}D^{\circ})4d \ ^{1}D_{2}^{\circ} \leftarrow 3s^23p^{4} \ ^{1}D_{2}$ transition using different gas pressures in the four-wave mixing cell with Scanmate 2 and FL2002 dye lasers. Different conversion efficiencies occur at these different pressures for frequency tripling that result in different VUV intensities. The absolute intensities at different Kr pressures vary by more than one order of magnitude. Figure 3 shows that the line profile does not change as the Kr pressure changes, which indicates that it is free from power broadening. The FWHM is a little different for the two dye lasers because of the different bandwidths of the lasers. The natural line width can be determined from these scans by assuming the dye lasers have Gaussian profiles, which have to be convoluted with the expected Lorentzian profile to produce the measured line shape. Figure 4 shows the fits obtained for the experimental line profiles using this convolution. The FWHM of the Lorentzian profiles obtained by these convolutions was 0.90 cm⁻¹ for scans using both Scanmate 2 and FL2002 dye lasers. Different Gaussian bandwidths of 0.5 and 0.9 cm⁻¹ have to be used in the convolution for the measurements using the Scanmate 2 and FL2002 dye lasers, respectively. The fits are excellent, and they yield a FWHM of $0.90 \pm 0.05 \text{ cm}^{-1}$ for the natural line width in both cases, which corresponds to an autoionization lifetime of 5.90 ± 0.31 ps. The bandwidths of the fundamentals of the two dye lasers are 0.09 and 0.16 cm⁻¹ for the Scanmate 2 and the FL2002, respectively. The VUV bandwidths obtained by tripling the doubling output of the dye lasers should be at most 6 times those for the fundamentals, which turn out to be 0.54 and 0.96 cm⁻¹, respectively. However, during the fitting it was found that the width of the Gaussian function for the FL2002 could be chosen between 0.9 and 1.2 cm⁻¹ to obtain a reasonable fit, with 0.9 cm⁻¹ producing the best fit. Similarly, the width of the Gaussian function for the Scanmate 2 could be chosen between 0.4 and 0.6 cm⁻¹, with 0.5 cm⁻¹ producing the best fit. The identical results for the natural line width from measurements using different dye lasers indicate the results are reliable.

Discussion

When an electron combines with the $3s^23p^3$ ion-core states of the sulfur atom, Rydberg series are formed whose energies converge to the associated ⁴S^o, ²D^o, or ²P^o ion states. The ⁴S^o core forms a series of triplet and quintet S, P Rydberg states, while ²D^o forms singlet and triplet P, D, F Rydberg states, and ²P^o forms singlet and triplet S, P, D Rydberg states. Photoabsorption and photoionization spectra of sulfur have been studied extensively in this region (3–5). Berkowitz and co-workers (5) reported the photoionization spectrum of sulfur in detail between the first ionization threshold and 92.5 nm. They assigned many of the autoionization states that converge to the ⁴S^o, ²D^o, ²P^o states of the S⁺ ion originating from the ground state of sulfur (³P₂) (5).

Even though there have been many studies on the photoionization of sulfur atoms and the autoionization levels for these sulfur atoms have been previously assigned, to our knowledge no autoionization lifetime measurements have been reported. On the other hand, there are measurements on the autoionization lifetimes 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 Edlen and Sven (17) and by Eriksson and Isberg (18). The transitions involving the ${}^{1}P_{1}$ level were broadened by approximately 0.2 cm⁻¹ with an autoionization lifetime of 3×10^{-11} s to the ${}^{4}S_{3/2}^{o}$ continuum; the transitions involving the ¹F₃ level were sharper, and hence the lifetimes were longer (18). Instances of forbidden autoionization in atomic oxygen have been discussed by Huffman et al. (19) and Dehmer and co-workers (20-22) for Rydberg states excited from the ³P, ¹D₂, and ¹S₀ lower states. Recently, Pratt et al. (23) reported the autoionization of O $(^{2}D^{o})3p$ $^{1}P_{1}$ and

Fig. 3. The line profiles obtained under different Kr pressures in the VUV cell (indicated on the figure in torr (1 torr = 133.322 Pa)) and using different dye lasers. The curves are individually normalized to 1 at the highest point. The absolute intensities differ by more than one order of magnitude at different pressures.



Fig. 4. The convolution fits of the experimental line profiles and the deconvoluted Lorentzian profile with a FWHM of 0.9 cm⁻¹ in both cases: (*a*) for measurements with the Scanmate 2 dye laser, whose fundamental bandwidth is 0.09 cm⁻¹, and (*b*) for measurements with the FL2002 dye laser, whose fundamental bandwidth is 0.16 cm⁻¹.



 ${}^{1}F_{3}$ levels excited from the O(${}^{1}D_{2}$) state by two-photon absorption. 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} and 5.8×10^{-10} s, respectively. Smith and co-workers (6, 7) have done a considerable amount of work on the autoionizing states of atomic oxygen. They measured the autoionization lifetimes for the $(^{2}D^{o})3p$ ^{1,3}P and $(^{2}D^{o})3p$ ³D, ³F states by measuring the Rabi oscillations that were induced when the atoms were excited from the ${}^{3}P_{2}$ ground state by the multiphoton process. The autoionization lifetimes are on the order of 10^{-10} s for all the states except the $(^{2}D^{\circ})_{3p}$ ³P state, which has a 6-fs lifetime (7). More recently, single-photon ionization of atomic singlet oxygen O $({}^{1}D_{2})$ was investigated by Flesch et al. (24). The photoionization efficiency spectrum was recorded between the onset of the first $({}^{4}S^{o})$ and the second $({}^{2}D^{o})$ ionization thresholds. However, no lifetimes were reported in this paper.

Within the LS coupling approximation, direct photoionization to the ${}^{4}S^{0} + e^{-}$ state between the first and the second ionization threshold (to $(^{2}D^{o})$) is optically forbidden from the singlet states of the atom, since it violates the spin conservation rule. Thus, the only way these states can be ionized is via autoionization to ⁴S^o as a result of spin-orbit, spin-spin, or other possible weaker interactions that couple atomic states with different spins (25-27). As discussed above, the lifetimes of the singlet states for atomic oxygen were found to be of the order of 10^{-10} s. In the current measurements for singlet atomic sulfur ¹D₂^o, the lifetime was determined as 5.9 ps. This much faster autoionization rate for sulfur ¹D₂^o compared with singlet oxygen atoms can be understood in terms of spin-orbit and spin-spin interactions. The mass of the sulfur atom is much greater than that of the oxygen atom; one would therefore expect that spin-orbit interaction in the heavier sulfur atom would be much stronger than in the oxygen atom. This is seen in the spin-orbit splittings that are observed in the ${}^{3}P_{2,1,0}$ ground state of the sulfur atom, which are 396 and 177 cm⁻¹ for ${}^{3}P_{1}$ - ${}^{3}P_{2}$ and ${}^{3}P_{0}-{}^{3}P_{1}$, respectively, whereas they are only 158 and 69 cm⁻¹ for the oxygen atom (28). The spin-spin interaction can also play an important role in the autoionization process. In the highly excited states, mixing between states with different spin is expected because of spin-spin interaction. The existence of state mixing between the very rapidly ionizing triplet state and the singlet state could promote the autoionizing rate of the singlet state.

The rate of autoionization, and the corresponding lifetime, can be estimated by the Golden Rule formula,

[1]
$$k = \frac{2\pi}{\hbar} \left| V_{\rm if} \right|^2 \rho_{\rm f}$$

where V_{if} is the transition matrix element and ρ_f is the density of the final states. The zeroth-order initial and final states are described in a SCF Breit–Pauli approximation (29) by neglecting spin–spin and spin–orbit interactions. In the initial state $3s^23p^3(^2D^\circ)4d$ ($^1D_2^\circ$), prepared by single-photon excitation, one electron occupies a 4*d* orbital, and the rest form an ionic core, whose electronic configuration, $3s^23p^3(^2D^\circ)$, corresponds to an excited state of the S⁺ ion. In the absence of spin–spin and spin–orbit interactions, the excited state is stable, with one 4*d* electron moving in a Coulomb field of the ionic core. The additional interaction between this electron and the core results in their energy exchange, a process in which the 4d electron is excited to an unbound state with kinetic energy sufficient to escape the Coulomb cage of the core, while the ionic core itself relaxes to its ground state of ${}^{4}S_{3/2}$. In the latter process, one of the electrons in the doubly occupied p orbital of the $3s^23p^3(^2D^\circ)$ configuration is transferred to an empty p orbital, simultaneously changing its spin, so that in the final state of the core all three electrons occupy three different p orbitals and have parallel spins, yielding $3s^23p^3$ S⁺(⁴S^o_{3/2}). Owing to the exchange effects, the same final state can be obtained by a transfer of the 4d electron to an empty orbital of the 3pshell, while one of the paired electrons from the 3p shell of the core is promoted to an unbound state and ejected from the atom. However, the contributions of the exchange effects in the latter type of interactions are typically small (29). The exact evaluation of the rate of the described process requires rather sophisticated computational work as, e.g., in ref. 30. However even a rough estimate described in the Appendix gives FWHM values in the range 10-40 cm⁻¹, which is about an order of magnitude higher than the experimental measurements.

Conclusion

For the first time, we are able to record the $3s^23p^34d {}^1D_2^{\circ} \leftarrow 3s^23p^{41}D_2$ transition line width of atomic sulfur using single VUV photon excitation by monitoring the S⁺ signal in a TOF-MS while scanning the excitation wavelength. The deconvolution of the measured excitation line shape with the finite laser bandwidth yields a natural line width (FWHM) of 0.90 ± 0.05 cm⁻¹, from which the autoionization lifetime of the neutral superexcited state $3s^23p^34d {}^1D_2^{\circ}$ is found to be 5.90 ± 0.30 ps. These results show that this is a general method to measure the lifetimes of atomic autoionization states with strong spin–orbit and spin–spin interactions.

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Appendix A

Here, we estimate the order of magnitude of the autoionization rate of the process described in the text, using experimental data for typical spin–orbit interactions in sulfur. The rate is given by the Golden Rule formula,

[A1]
$$k = \frac{2\pi}{\hbar} \left| V_{\rm if} \right|^2 \rho_{\rm f}$$

where V_{if} is the transition matrix element, and ρ_f is the density of the final states. The final states result from the ionized electron moving in the field of the ionic core. The number of such states is given by the usual expression:

[A2]
$$dn = V \frac{d\vec{p}}{(2\pi\hbar)^3}$$

where V is the volume of the system, and \vec{p} is the momentum of the ejected electron. Integration over all directions gives the density of states,

$$[A3] \quad \rho = V \frac{m}{\pi^2 \hbar^3} \sqrt{\frac{mE}{2}}$$

where *E* is the kinetic energy of the ejected electron $(E({}^{1}D_{2}^{o}) - IP; about 1 eV)$. The exit state of the ejected electron should be described by a wave function of an electron moving in the field of the ionic core. For a rough estimate, however, we will take

$$[A4] \quad \left| \vec{p} \right\rangle = \frac{1}{\sqrt{V}} \exp\left(\frac{i\vec{p}\vec{r}}{\hbar}\right)$$

For an estimate of the matrix element, we can then write

$$[A5] \quad V_{\text{if}} = \langle \varphi_{3\,px}^{\downarrow}(1) \varphi_{4d}^{\uparrow}(2) \middle| \hat{V}(1,2) \middle| \varphi_{3\,pz}^{\uparrow}(1) \vec{p}(2) \rangle \approx \overline{V}_{12} \frac{a_{4d}^{3/2}}{\sqrt{V}}$$

where a_{4d} is the radius of the 4*d* orbital, and \overline{V}_{12} is the average spin–spin and spin–orbit interactions between the 4*d* electron and electrons of the 3*p* shell of the core. The exchange effects should not change the order of magnitude of the above estimate. Here, we neglect factor $2\sqrt{2}/\pi$, which is on the order of unity. Thus, for the rate we roughly have

$$[A6] \quad k \approx \frac{\overline{V}_{12}^2}{2\hbar} \frac{a_{4d}^2 m}{\hbar^2} \frac{a_{4d}}{\hbar} \sqrt{mE}$$

The last term in the above expression is roughly the angular momentum of the ejected electron; since the kinetic energy of the electron is about 1 eV, the last term gives a factor close to 4. The second term is the inverse kinetic energy of the 4d electron, the order of magnitude of which is also 1 eV. A typical value of spin-orbit interaction in the sulfur atom can be estimated from the splittings of the ${}^{3}P_{2}-{}^{3}P_{1}$ (396 cm^{-1}) and ${}^{3}P_{1}-{}^{3}P_{0}$ (177 cm⁻¹) energy levels of the ground state (A1). For $\overline{V_{12}} = 200 \text{ cm}^{-1}$, the FWHM is estimated to be 10 cm⁻¹; for $\overline{V_{12}} = 400 \text{ cm}^{-1}$, FWHM = 40 cm⁻¹. Given the crude nature of the estimate, it is not surprising that the estimation is an order of magnitude higher than the observed value. Note that the term $\overline{V_{12}}$ in eq. [A5] should be the interaction between the 4d Rydberg electron and the 3pcore electrons. Considering the large diameter of the Rydberg orbital, the interaction \overline{V}_{12} should be much weaker than that in the ground state $S(^{3}P)$. Using the measured line width of 0.9 cm⁻¹, we can estimate \overline{V}_{12} to be 60 cm⁻¹.

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