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Velocity map imaging studies of the photodissociation of CS₂ by two-photon excitation at around 303–315 nm

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ABSTRACT

Two-photon dissociation dynamics of carbon disulfide (CS₂) have been studied by using the timesliced velocity map ion imaging technique. Images of the S (¹D₂) and S (³P₀) photoproducts formed in the CS₂ photodissociation are acquired at four photolysis wavelengths from 303 nm to 315 nm. Vibrational states of the CS co-products are partially resolved and identified in the images. The CS (X¹ Σ ⁺) products are highly vibrationally excited with moderate rotational excitation. The spin–orbit state-specific dissociation dynamics are also investigated by measuring the images of three S (³P_J) spin–orbit states (J=0, 1, and 2) at photolysis wavelength 303.878 nm. The branching ratios of CS (a³ Φ)/CS (X¹ Σ _g⁺) are determined to be 0.05 ± 0.02, 0.17 ± 0.04, and 0.26 ± 0.05 for the three spin–orbit states S (³P₀), S (³P₁), and S (³P₂) respectively, implying a strong spin–orbit coupling exists in the dissociation process. The averaged anisotropy parameters $\beta_2 > 0$ and $\beta_4 \sim 0$ suggest that the CS₂ molecules undergo a sequential transition 2¹B₂(2¹ Σ ⁺) \leftarrow 1¹B₂(¹ Δ_u) \leftarrow X¹ Σ _g⁺ with the intermediate state 1¹B₂ having a long lifetime, followed by nonadiabatic and spin–orbit couplings to other electronic states and then dissociate.



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Introduction

Carbon disulfide (CS₂) is a linear triatomic molecule with 16 valence electrons, its structure and photodissociation behaviour are similar to that of the previously studied N₂O and OCS [1,2]. CS₂ is a prototype molecular system to study the evolution of wave-packets on complex potentials, such as in the vicinity of conical intersections [3,4]. In addition, CS₂ is an important molecule in several comets, which is regarded as the parent of CS and S₂ radicals in comets [5,6]. In the past few decades, photodissociation dynamics of CS₂ have been extensively investigated either theoretically or experimentally.

The strongest absorption band of CS₂ occurs in the region from 188 to 210 nm, which results from the excitation of the predissociative ${}^{1}B_{2}({}^{1}\Sigma_{u}^{+})$ state from the linear ground state X (${}^{1}\Sigma_{g}^{+}$). Absorption of one photon in this region results in the production of singlet CS (X¹ Σ^+) fragments and sulfur atoms in the singlet or triple state $(^{1}D \text{ or }^{3}P)$ [7–13]. The branching ratio for the S (³P) and S (¹D) channels reported from these studies varies widely, from 0.25 to 6 [7-10]. It seems to settle down to 3 in favour of the triple state, but recent studies using velocity map ion imaging have reported branching ratios of 1.5 ± 0.4 by Kitopoulos *et al.* [14], and 1.6 ± 0.3 by Xu et al. [15], at the photolysis wavelength of 193 nm. There has also been significant work on the CS state distributions and fragment translational energy distributions. The CS fragment was observed in vibrational levels up to v = 13 with a maximum near v = 3 [12,16,17]. The rotational distributions cannot be described by a single temperature and yielded an average rotational energy of 1–3 kcal/mol for CS fragments with $v \le 5$ but significantly higher for v > 5.

For photolysis wavelengths towards the vacuum ultraviolet (VUV) region, the following channels become energetically accessible:

 $CS_2 + h\nu \rightarrow CS(X^1\Sigma^+) + S(^3P_J)$ $D_{Th} = 4.46eV$ (1)

$$\rightarrow CS(X^{1}\Sigma^{+}) + S(^{1}D_{2}) \quad D_{Th} = 5.61 \text{eV}$$
(2)

$$\rightarrow \mathrm{CS}(\mathrm{X}^{1}\Sigma^{+}) + \mathrm{S}(^{1}\mathrm{S}_{0}) \quad D_{\mathrm{Th}} = 7.21\mathrm{eV}$$
(3)

$$\rightarrow CS(a^{3}\Phi) + S(^{3}P_{J}) \quad D_{Th} = 7.88eV$$
(4)

The threshold energies (D_{Th}) of these channels are adapted from Ref. [1]. The channel (4) becomes more important with the photolysis wavelength decreases, and between 140–125 nm, the CS fragments are almost completed produced in the triplet state [18]. Besides, CS₂ shows a strong absorption band around 340–290 nm, which has been assigned to the ${}^{1}B_{2} \leftarrow X^{1}\Sigma_{g}^{+}$ transition [19]. This ${}^{1}B_{2}$ upper state is bent with an \angle SCS angle of 131° and correlates to the ${}^{1}\Delta_{u}$ valence state

in the linear configuration. One-photon excitation of CS_2 at ~300 nm (4.13 eV) cannot lead to dissociation. The CS photoproducts are formed by the sequential (1+1) absorption of two photons via the ${}^{1}B_{2}$ intermediate state to a predissociative excited state lying near 150 nm [20]. In the last few years, numerous studies on the photodissociation of CS₂ in this region via two-photon absorption have been reported. Hardwick et al. [21] used resonance-enhanced multiphoton ionisation (REMPI) detection of the photoproducts combined with time-of-flight (TOF) analysis to study the two-photon dissociation of CS₂ between 330-280 nm. Based on their experimental observations, they were able to identify the channel (4), but were unable to speculate on the importance of the other channels. Kawasaki et al. [22,23] identified the spin-orbit electronic state of the S-atom products by REMPI detection, and measured the speed and angular distributions of nascent sulfur fragments. They elucidated that the intermediate ${}^{1}B_{2}$ state reached after the first one-photon absorption has a quite long lifetime. Donaldson and coworkers [24] observed the vibrationally hot CS ($X^{1}\Sigma^{+}$) products but could not distinguish the $CS(X^{1}\Sigma^{+}) + S(^{3}P_{I})$ channel and the $CS(X^1\Sigma^+) + S(^1D_2)$ channel due to the absence of translational energy release measurement. Recently, Kitsopoulos et al. [25] studied two-photon dissociation of CS₂ at 69,399, 64,893, 64,496, and $64,320 \text{ cm}^{-1}$ by using the ion imaging technique. From the S-atom photoproduct translational energy distribution they concluded that CS is produced in both the $X^1\Sigma^+$ and $a^3\Phi$ states with a branching ratio CS $(a^{3}\Phi) + S (^{3}P_{2})/CS$ $(X^{1}\Sigma^{+}) + S(^{3}P_{2})$ of 0.22 ± 0.05 at 64,893 cm⁻¹. However, because of the limited experimental resolution, the state-resolved dynamics of CS₂ by two-photon excitation around 300 nm remains unclear.

In this work, we report the photodissociation dynamics of CS_2 through two-photon excitation at around 303–315 nm by using the time-sliced velocity map ion imaging technique. By detecting the ion images of S photoproducts, the channels (1), (2) and (4) are clearly observed. The vibrational structures of the CS coproducts are partially resolved in the experimental images. The study of these channels can possibly be beneficial in the study of non-adiabatic photodissociation dynamics.

Experimental methods

The apparatus for velocity map ion imaging (VMI) experiments has been described previously [26–29]. Briefly, a supersonic molecular beam of CS₂ (0.3% seeded in He) is generated by a General Valve (Parker Series 9, operated at 20 Hz) with a 1 mm orifice. After being collimated by a 1.5 mm diameter skimmer, the CS₂ molecular beam is introduced into the detection chamber. The detection chamber has a typical operation pressure of 5×10^{-8} Torr.

The laser system consists of two Nd:YAG Lasers and four dye lasers. A UV laser beam (\sim 300 nm) generated by frequency doubling the output of an Nd:YAG (Spectra Physics, PRO-200) laser pumped dye laser (Corbra-Stretch, Sirah) is used to photolyze the CS₂ molecules. The second Nd:YAG (Continuum, Powerlite 9030) laser is employed to pump three dye lasers (Corbra-Stretch, Sirah) simultaneously, which is designed to generate the 1 + 1' (VUV + UV) detection beams of S(³P_I) atom products, while $S(^{1}D_{2})$ atoms are excited by only one VUV laser beam to the autoionisation level [29]. The VUV light beam (\sim 130 nm) is generated by the fourwave mixing $(\omega_{VUV} = 2\omega_1 - \omega_2)$ cell. The laser light at 212.55 nm (ω_1) is generated by the doubling of the fundamental output of the dye laser 1, which is pumped by the 355 nm laser light generated by the second Nd: YAG laser. The second harmonic output (532 nm) of the Nd:YAG laser is used to pump the dye laser 2, the output of which is used as the laser light ω_2 (~580 nm). The two laser beams at the frequencies of ω_1 and ω_2 are spatially and temporally overlapped and focused into a stainless-steel mixing cell filled with Krypton. Due to the large background caused by the 212.55 nm light crossing the photodissociation region, a biconvex LiF lens (f = 120 mmat 212.55 nm) is used to make this light off the reaction centre. The fundamental frequency output from the dye-laser 3 (ω_3 , another UV light) is employed as the detection light (1') for detecting S $({}^{3}P_{I})$ atoms. All lasers mentioned above are fixed at the horizontal plane and thus parallel to the detector's front plane, and so do their polarisation directions.

The molecular beam is 90° crossed by the photolysis and detection laser beams at the reaction centre, which locates between the second and the third plates of the ion optics assembly. After two-photon dissociation of CS2 molecules, S (1D₂, 3P_J) atom products are state-selected ionised by the detection beams, followed by accelerating directly to the detector via the ion optics. Then the S⁺ ions impact on the 70 mm-diameter microchannel plate (MCP) detector coupled with a phosphor screen (P43). A charge-coupled device (CCD) camera is used to record the images on the phosphor screen, using a 15 ns gate pulse voltage in order to acquire time-sliced images. Time controlled system consists of two Delay Generators (DG645 Stanford Research System). The Doppler scanning of ω_2 is carried out to measure S atom products with different velocities.

Results and discussion

As mentioned above, we employed two-photon excitation of CS_2 in the wavelength region of 303–315 nm (*i.e.*

the two-photon energies from 8.18 eV to 7.87 eV), and the VUV or VUV + UV beams to ionise the S atom products. This strategy suppressed some multi-photon dissociation or ionisation processes, thus improved the translational energy resolution. Figures 1 and 2 present the ion images of S $({}^{1}D_{2})$ and S $({}^{3}P_{0})$ products at photolysis wavelengths 303.878, 307.322, 312.983, and 314.545 nm, respectively. The double headed red arrows in the figures stand for the polarisation direction of photolysis lasers. Partially resolved concentric ring structures are observed in the ion images of S $({}^{1}D_{2})$ and S $({}^{3}P_{0})$ products, which correspond to individual vibrational states of coproduct CS ($X^1\Sigma_g^+$), respectively. In addition, the inner bright rings in the ion images of S $({}^{3}P_{0})$ at 303.878 nm and 307.322 nm can be ascribed to vibrational states of coproduct CS ($a^{3}\Phi$). The total translational energy spectra for the dissociation products in both the S $(^{1}D_{2})$ and S $({}^{3}P_{0})$ product channels were derived by integrating the signal in the image over the full angular ranges. Based on the law of momentum conservation and energy conservation, the translational energy releases (TERs) for the photolysis products can be described by the following equation:

$$\text{TER} = E_{h\nu} - D_0(\text{CS} - \text{S}) - E_{\text{int}}(\text{CS}) - E_{\text{int}}(\text{S}) \quad (5)$$

where $E_{h\nu}$ is the energy of the photolysis laser, D_0 (CS-S) is the bond energy, which has been determined by previous studies [30], E_{int} (CS) is the internal energy of CS products, and E_{int} (S) is the energy difference between the sulfur atom products and the ground state S (³P₂).

The translational energy distributions in the centreof-mass frame are shown in the right panels of Figures 1 and 2. The spectra show a clear yet diffuse progression which can be assigned to the vibrational states of the CS coproducts. It is noted that the S $(^{1}D_{2})$ channel has more clear structures than the S $({}^{3}P_{0})$ channel due to the less internal energy in the former process. The energy combs representing the vibrational quantum numbers v of CS $(X^1 \Sigma_g^+)$ and CS $(a^3 \Phi)$ products are labelled in Figures 1 and 2. To abstract more information, a qualitative simulation of the energy distribution was carried out. Considering the partially resolved peaks showing relatively uniform intervals, we assume the rotational state distributions of CS are Boltzmann distributions. Each vibrational peak was simulated using a Gaussian-like shape with a little changed linewidths. The simulation reveals that the CS is not highly rotationally excited in both S $(^{1}D_{2})$ and S $({}^{3}P_{0})$ channels. The moderate rotational temperature $(\sim 1600 \text{ K})$ of the CS $(X^1 \Sigma_g^+)$ products suggests that the transition state is close to a linear geometry for the dissociation process. While the averaged rotational temperature of the CS $(a^3 \Phi)$ is relatively cold with the value \sim 700 K.



Figure 1. Ion images and translational energy distributions (arb. units) of S (¹D₂) products from two-photon dissociation of CS₂ at wavelengths (a) 303.878 nm, (b) 307.322 nm, (c) 312.983 nm, and (d) 314.545 nm. The rings shown in the images correspond to the vibrational state of the CS ($X^1\Sigma^+$) co-products.

Figures 3 and 4 show the relative vibrational state populations of CS products. The CS $(X^1\Sigma_g^+)$ products are highly vibrationally excited, with the largest population at v = 11, 12, 13, and 14 for the S (¹D₂) channel with the photolysis wavelength 314.545 nm, 312.983 nm, 307.322 nm, and 303.878 nm, respectively. The CS $(X^1\Sigma_g^+)$ products for the S $({}^3P_0)$ channel show quite similar distributions at all four wavelengths. The vibrational state population maximises at v = 18-21 and extends to around v = 24-26, due to more available energy in the S $({}^{3}P_{0})$ channel. Furthermore, a narrow peak at very low kinetic energy region at 307.322 nm is assigned to the CS ($a^{3}\Phi$) products with v=0, suggesting the excitation energy is just well above the threshold energy of the channel (4). At 303.878 nm, the population of the CS ($a^3\Phi$) products is significantly increased, which

Figure 2. Ion images and translational energy distributions (arb. units) of S $({}^{3}P_{0})$ products from two-photon dissociation of CS₂ at wavelengths (a) 303.878 nm, (b) 307.322 nm, (c) 312.983 nm, and (d) 314.545 nm. The outer rings shown in the images at four wavelengths correspond to the vibrational state of the CS ($X^1 \Sigma^+$) co-products, while the inner rings at (a) and (b) images correspond to the vibrational state of the CS $(a^3 \Phi)$ co-products.

24000

24000

24000

24000

32000

32000

32000

32000

is in accord with that observed in the shorter wavelengths in the VUV region [18].

To address the spin-orbit state-specific dissociation dynamics, we have acquired S $({}^{3}P_{I})$ images for the three spin-orbit states (J=0, 1, and 2). Figure 5 displays the ion images of S (³P₀), S (³P₁), and S (³P₂) products and their corresponding translational energy distributions from two-photon dissociation of CS2 at wavelength 303.878 nm. It is noted that all three images, shown in the same display resolution, are divided into two different regions: the inner bright rings correspond to the product CS ($a^{3}\Phi$), and the outer dark rings represent the product CS ($X^1\Sigma_g^+$). The TKERs show a dramatic change of the relative intensity of CS ($a^{3}\Phi$) and CS ($X^{1}\Sigma_{g}^{+}$) products with the S $({}^{3}P_{I})$ spin-orbit state being probed from J = 0



Figure 3. Relative population of different vibrational states of the CS ($X^1 \Sigma^+$) co-products of S (1D_2) at four photolysis wavelengths.



Figure 4. Relative population of different vibrational states of the CS ($X^1\Sigma^+$) co-products of S (3P_0) at four photolysis wavelengths, and CS ($a^3\Phi$) co-products at 303.878 and 307.322 nm, respectively.

to J = 2, suggesting a strong spin-orbit coupling exists in the non-adiabatic dissociation processes.

Figure 6 displays the relative populations of different vibrational states of the CS ($a^{3}\Phi$) and CS ($X^{1}\Sigma_{g}^{+}$) products with the S $({}^{3}P_{I})$ spin-orbit state J = 0, 1 and 2. A little hotter vibrational excitation of CS ($X^1\Sigma_g^+$) products has been observed for the S $({}^{3}P_{2})$ channel, with the maximum population at v = 25. The most prominent phenomenon is the dramatic change of the relative intensity of the CS $(a^{3}\Phi)$ products with the S $({}^{3}P_{I})$ spin-orbit state being probed from J=0 to J=2. The branching ratios of CS $(a^{3}\Phi)/CS$ $(X^{1}\Sigma_{g}^{+})$ are $0.05\pm0.02,\ 0.17\pm0.04,\ and\ 0.26\pm0.05$ for the three spin-orbit states S (³P₀), S (³P₁), and S (³P₂) respectively. The results are similar to that reported in the previous studies, in which the branching ratio of 0.22 for the S $({}^{3}P_{2})$ channel was obtained at around 308 nm [25]. These results imply that the coupling between the singlet and triplet states that induces different spin-orbit pathways



Figure 5. Ion images of the S (${}^{3}P_{J=0,1,2}$) products from twophoton dissociation of CS₂ at 303.878 nm. The ring features in the outer and inner portion of three images correspond to the vibrational states of the CS (X¹ Σ^+) and CS ($a^{3}\Phi$) co-products, respectively.



Figure 6. Relative population of different vibrational states of the CS ($X^1 \Sigma^+$) and CS ($a^3 \Phi$) co-products of S (${}^{3}P_J$) at the photolysis wavelengths 303.878 nm, where J = 0, 1, 2, respectively.

might be a little different, thus causing slightly different dynamics for the different spin-orbit dissociation channels.

The product spatial angular distribution was also obtained by the following equation:

$$I(\theta_s) = \sigma \{1 + \beta_2 P_2(\cos \theta_s) + \beta_4 P_4(\cos \theta_s)\}$$
(6)

where σ is the product translational energy distribution, β_2 and β_4 are anisotropy parameters which depend on



Figure 7. Differential cross sections for the S (${}^{1}D_{2}$, ${}^{3}P_{0,1,2}$) photoproducts following two-photon dissociation of CS₂, obtained by integrating the outer portion of the ion images (while full image of S (${}^{1}D_{2}$)): (•) experimental point, (–) simulation by equation 6.

the details of the excitation and the decay of the molecule, P_2 and P_4 are Legendre polynomials, and θ_s is the scattering angle. The overall angular parameters were determined by fitting the angular distributions in Figure 7. Table 1 lists the overall anisotropy parameters of S $(^{1}D_{2})$ products at four photolysis wavelengths. The averaged β_2 values over the product translational energy distribution are 0.66, 0.63, 0.61, and 0.68 for S (¹D₂) products at the wavelengths 303.878, 307.322, 312.983, and 314.545 nm respectively. Within the experimental error, they are almost same. While the averaged β_4 values are close to zero at four wavelengths. According to previous studies, the absorption band in the region 290-330 nm of CS₂ has been assigned as V-band, corresponding to ${}^{1}B_{2}$ (${}^{1}\Delta_{u}$) $\leftarrow X^{1}\Sigma_{g}^{+}$ transition [19,31]. This ${}^{1}B_{2}$ state has a quite long lifetime, thus the angular distribution is determined solely by the second transition from the intermediate ${}^{1}B_{2}$ state to the final state, and the coherence between the first and the second photons would not be important [22]. Arikawa and co-workers suggested the β_4 could be ignored [23]. By setting β_4 to be zero, they obtained the β_2 values to be 0.88 \pm 0.08. The parameter values observed in this work are in fair agreement with Arikawa's results.

Table 2 lists the averaged anisotropy parameters for the S (${}^{3}P_{J=0,1,2}$) products at 303.878 nm. For the CS (X ${}^{1}\Sigma_{g}^{+}$) coproducts, the values are similar to that observed in the S (${}^{1}D_{2}$) product channel, with the β_{2} value of

Table 1. The anisotropy parameter values derived from simulations of differential cross sections for S $(^{1}D_{2})$ photoproducts by using equation 6.

Wavelengths / nm	β_2	β_4
303.878	0.66	0.04
307.322	0.63	-0.002
312.983	0.61	0.002
314.545	0.68	0.008

Table 2. The anisotropy parameter values derived from simulations of differential cross sections for S $({}^{3}P_{2,1,0})$ photoproducts.

channels	β ₂	β_4
$\overline{S(^{3}P_{2})+CS(X^{1}\Sigma^{+})}$	0.59	-0.03
$S(^{3}P_{2}) + CS(a^{3}\Phi)$	0.32	0.01
$S(^{3}P_{1}) + CS(X^{1}\Sigma^{+})$	0.57	-0.01
$S(^{3}P_{1}) + CS(a^{3}\Phi)$	0.38	0.02
$S(^{3}P_{0}) + CS(X^{1}\Sigma^{+})$	0.72	0.03
$S(^{3}P_{0}) + CS(a^{3}\Phi)$	0.28	0.03

around 0.6–0.7 and the β_4 value of around 0. In contrast, the β_2 value is slightly smaller (~0.3) for the CS ($a^3\Phi$) coproducts, suggesting a little slower (compared to the molecular rotation period) dissociation process.

The key to understanding the dissociation mechanisms of CS_2 is the detailed information of potential

energy surfaces (PESs). Recently, Francisco and coworkers [30] have constructed the PESs along the CS and SS bond lengths and along the bending angle. There is a high density of excited electronic states located at energies above 3 eV, characterised by an electron promotion from the outermost $2\pi_g$ molecular orbital (MO) to the vacant $3\pi_{\rm u}$ or $7\sigma_{\rm g}$ MO. Such high density of electronic states causes the mixing of their wavefunctions by vibronic coupling and spin-orbit interactions, leading to complex electronic and rovibrational spectra. In this work, the excitation photon energies are above 7.8 eV, which means that about six PESs can be reached in this region [30]. At large CS distances, the $^{3}\Sigma^{-}$ and $1^{3}\Phi$ electronic states correlate to the S $({}^{3}P)$ + CS $(X^{1}\Sigma_{g}^{+})$ dissociation limit, while the ${}^{1}\Delta$ and ${}^{1}\Phi$ states relate to S (${}^{1}D$) + CS $(X^1\Sigma_g{}^+),$ and the ${}^1\Sigma^-,\,{}^3\Sigma^+$ and ${}^3\Delta$ states relate to S $({}^{3}P) + CS(a{}^{3}\Phi)$. The $1{}^{3}\Phi$ electronic state has a repulsive character and forms an avoided crossing with the $2^{3}\Phi$ state, which correlates to S $({}^{3}P) + CS (a^{3}\Phi)$. There is a second ${}^{1}\Sigma^{+}$ state (i.e. $2{}^{1}\Sigma^{+}$) lying above 7.08 eV crossed by several singlet and triplet states in the molecular region. This electronic state can be efficiently populated from CS₂ (X¹ Σ_g^+) after the absorption of UV light. The positive anisotropy parameter observed in our experiment indicates a parallel transition $({}^{1}B_{2} \leftarrow {}^{1}B_{2})$ from the intermediate state. This makes ${}^{1}B_{2}$ type upper states (like $2^{1}B_{2}(2^{1}\Sigma^{+})$) suitable candidates for the upper electronic state involved in the photodissociation process. Kitsopoulos and coworkers [25] also suggested other electronic states ${}^{3}\Delta_{u}$ and ${}^{3}\Sigma_{u}^{+}$ contribute to the dissociation process, if the π_u bending mode of CS₂ are involved in the excitation process.

Thus, the two-photon excitation process in this work might be ${}^{1}B_{2}(2^{1}\Sigma^{+}) \leftarrow {}^{1}B_{2}({}^{1}\Delta_{u}) \leftarrow X^{1}\Sigma^{+}$. The moderate rotational excitation of CS products implies that such transition should be close to the linear geometry, rather than ${}^{1}B_{2}$ bent equilibrium geometry. From the closely-packed nature of the electronic states in the excitation region, one would expect rapid redistribution of the excited population via nonadiabatic and spin-orbit coupling in the early stages of the dynamics. For instance, the second ${}^{1}B_{2}$ (2 ${}^{1}\Sigma^{+}$) electronic state is crossed by the $1^{1}\Phi$ state for the linear configuration (with the energies of \sim 7 eV). After UV absorption, the S (¹D) + CS $(X^1\Sigma_g^+)$ products can be formed through vibronic coupling with $1^{1}\Phi$. In addition, S (³P) + CS (X¹ Σ_{g}^{+}) products can occur after spin-orbit coupling with the ${}^{3}\Phi$ electronic states. Similarly, S $({}^{3}P)$ + CS $(a^{3}\Pi)$ products can also occur after spin-orbit coupling with the $2^3\Pi$ states and/or vibronic coupling with $2^{1}\Delta$, $2^{1}\Pi$ states. The $2^{1}\Delta$, $2^{1}\Pi$ and $2^{3}\Pi$ states have relative deeper potential wells, in contrast to a repulsive PES of the $1^3\Pi$ electronic state, leading to the slightly different β_2 values for the CS $(a^{3}\Pi)$ and CS $(X^{1}\Sigma_{g}^{+})$. In the photodissociation process of CS₂, the nonbonding electrons of both S atoms contribute to the absorption and both C–S bonds are excited and stretched. Thus, if one C–S bond breaks, the other is highly vibrationally excited.

Conclusion

Two-photon dissociation of CS₂ in the wavelength range from 303 to 315 nm has been investigated by using velocity map ion imaging technique. Images of atomic sulfur ion products are obtained, from which the product channels: CS $(X^1\Sigma^+)$ + S $({}^3P_0)$, CS $(X^1\Sigma^+)$ + S $({}^1D_2)$ and CS $(a^{3}\Phi) + S(^{3}P_{0})$ are identified. Besides, the translational energy distributions and angular parameters as well as branching ratios between different vibrational states are derived. The CS $(X^1\Sigma^+)$ products are highly vibrationally excited with moderate rotational excitation. A dramatic change of the relative population between CS $(a^{3}\Phi)$ + S $(^{3}P_{I})$ and CS $(X^{1}\Sigma^{+})$ + S $(^{3}P_{I})$ channels is observed with the S (³P_I) spin-orbit state being probed from J=0 to J=2. With the analysis of the experimental results, the second ${}^{1}B_{2}$ $(2^{1}\Sigma^{+})$ state should play an important role in the photodissociation processes occurring at excitation energies in this work. These results will help us to understanding the nonadiabatic dissociation dynamics of CS₂ in the high excited electronic states.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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