

Ultrafast dynamics and dissociative ionization of CS₂ molecules studied via the femtosecond pump-probe method

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The ultrafast dynamics and dissociative ionization of CS₂ were studied using the pump-probe method with time-of-flight mass spectroscopy. The transient behavior of both parent ion (CS₂⁺) and fragment ions (S⁺ and CS⁺) was observed. It was found that all the ionic signals decay exponentially with lifetimes that were different for delay times, $t > 0$ and $t < 0$, which can be attributed to the evolution of different Rydberg states pumped by 267-nm and 400-nm laser pulses. The lifetimes of two Rydberg states were obtained simultaneously from one fitting of the transients. The fragment ions were produced by the dissociation of CS₂⁺, and it is suggested that the final ionic state is the C²Σ_g⁺ state of CS₂⁺ based on the measured S⁺/CS⁺ branching ratio. The S⁺/CS⁺ ratio is dependent on the delay time of the two lasers, indicating that the dissociation process of CS₂⁺ is related to the evolution of the intermediate Rydberg state.

ultrafast dynamics, femtosecond, pump-probe, carbon disulfide

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Photo-induced dynamics of polyatomic molecules has been of area of research of great interest for many years. With the advent of the ultrafast laser technology and the pump-probe method, one can “see” the making and breaking of the molecular bonds, and can follow the flow of energy and charge within molecular systems in real time. Since the pioneering ultrafast study of photodissociation of ICN was carried out by Zewail et al. in the late 1980s [1], there has been a lot of work using the femtosecond time-resolved pump-probe method to provide a wealth of knowledge of the photophysics and photochemistry of isolated molecules and molecular clusters [2–6], as well as those in solution [7], solid phase [8] and light-harvesting complexes [9].

Carbon disulfide (CS₂) is a prototypical triatomic molecule, which plays an important role in stratospheric chemistry. CS₂ has been the subject of high-resolution spectroscopic measurements and photodissociation dynamics studies for

many years. Rich information on the first five electronic excited states of neutral CS₂ in the wavelength range of 290–410 nm has been obtained [10]. Efforts have also been made to understand the structure and non-adiabatic dynamics of the predissociation ¹B₂(¹Σ_u⁺) state over the wavelength range 180–230 nm. These include high-resolution absorption [11], resonance enhanced multiphoton ionization (REMPI) [12] and laser induced fluorescence [13] spectroscopic studies, and dynamic studies [14], to determine the channel branch ratio, the fragment energy partition, and the lifetime. Rydberg series were investigated in a wide range of excitation energies using the (2+1) and (3+1) REMPI methods [15]. In addition to the neutral CS₂ molecule, the structure and dynamics of the ground and excited ionic state, CS₂⁺, have been investigated by several groups, using synchrotron-based pulse-field-ionization photoelectron spectroscopy [16], the photoelectron photoion coincidence technique [17], photofragment excitation spectroscopy [18–20], and the optical-optical double resonance technique

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[21]. These spectroscopic and dissociation studies demonstrated that CS₂ exhibits many typical physical processes within molecular system, such as spin-orbit coupling, Fermi resonance, intersystem crossing and internal conversion. Consequently, despite numerous existing studies, CS₂ is still attracting more attention to reveal detailed information about these dynamics.

In contrast to the abundance of spectroscopic and photo-dissociation studies, ultrafast time-resolved investigations of CS₂ are relatively rare. The first ultrafast experiment on predissociation ¹B₂(¹Σ_u⁺) state was made by Baronavski et al. [22] using femtosecond pump-probe ion-yield measurements at an excitation wavelength of 205 nm. They reported lifetimes of (600±100) fs. Later, Farmanara et al. [23] carried out a more expansive time-resolved study over the wavelength range 194–207 nm, and observed lifetimes between 180 fs and 620 fs. An almost constant lifetime of 400 fs was found around 200 nm. Townsend et al. [14] proposed a more insightful investigation of the ¹B₂(¹Σ_u⁺) state decay dynamics by employing femtosecond time-resolved photoelectron spectroscopy (TRPES). More recently, Bisgaard et al. [24] carried out work on the time-resolved molecular frame dynamics of fixed-in-space CS₂ molecules. They first used a short (100 fs), nonresonant (805 nm) laser pulse to align the molecule, and then followed this with a pump-probe scheme with photoelectron imaging measurement. The dynamics of Rydberg states of CS₂ molecules were investigated by Liu et al. [25] using time-resolved pump-probe ion yield measurement, and by Knappenberger et al. using TRPES technique [26,27].

In this paper, we report an experimental study of the ultrafast dynamics and dissociative ionization of CS₂ by means of time-of-flight (TOF) mass spectroscopy. In contrast to all previous ultrafast time-resolved studies, where only the parent ions were investigated, we observed the transient behavior of both parent ion (CS₂⁺) and fragment ions (S⁺ and CS⁺). The lifetimes of two intermediate Rydberg states pumped by 267-nm (for delay time $t > 0$) and 400-nm ($t < 0$) lasers were obtained simultaneously from one pump-probe experiment using the best fit of the transient components. The dissociative ionization of CS₂ is discussed in terms of the measured S⁺/CS⁺ branching ratio, and the results indicate that the dissociation process of CS₂⁺ is related to the evolution of the intermediate Rydberg state.

1 Experimental

The experimental setup was similar to those described in our previous studies [28–30]. Briefly, CS₂ molecules were pumped to an excited state by a femtosecond laser pulse, and then were ionized by another femtosecond laser pulse. Cationic signals with various delay times between the two laser pulses were recorded using a TOF mass spectrometer

with an ion optical system based on the Wiley-McLaren design. CS₂ samples were purchased from J&K Chemica (Beijing, China) (99% purity) and were used without further purification. The samples were mixed with the carrier gas, He, at room temperature. The jet cooled CS₂ molecules were produced from the supersonic expansion of the CS₂-He mixture through a pulsed nozzle (General Valve, G9, New Jersey, USA) into a vacuum chamber. The stagnation pressure was kept at about 1 atm, and the operating pressure in the chamber was 3×10⁻⁶ Torr.

The laser system was a Ti:Sapphire chirped-pulse amplified laser with a central wavelength of 800 nm, pulse duration of 90 fs and repetition rate of 10 Hz. The maximum pulse energy of the laser system at 800 nm is 2 mJ. The outputs of the second harmonic (400 nm) and the third harmonic (267 nm) were used as pump-probe laser pulses. The 267-nm laser pulse was introduced to TOF mass spectrometer via a quartz lens, while the 400-nm laser pulse was directed by a motor-controlled delay stage. The two laser beams were recombined collinearly using a dichroic beam splitter, and were focused by a lens with a focal length of 250 mm prior to entering the interaction region. A half-wave plate and a Glan prism were inserted into each laser beam as a means of varying laser intensity. The laser intensities used in this work at 267 nm and 400 nm were estimated to be 4×10¹² and 2×10¹³ W/cm², respectively. The ions produced were extracted and accelerated by optical ion lens and were detected using dual micro-channel-plates at the end of the 1-m flight. The mass resolved ion signals were amplified with a pre-amplifier and then were recorded and averaged using a computer-controlled GPIB card. The TOF mass spectrum at fixed-delay time was averaged over 1000 laser shots.

2 Results and discussion

2.1 TOF Mass spectra at “time zero”

One purpose of this study is to investigate ionization/dissociation of CS₂ molecules in femtosecond laser fields. Therefore, we carefully controlled the intensity of each laser pulse, so that both parent CS₂⁺ and fragment ions can be measured as a function of pump-probe delay time, and their ion yields could be reduced to the greatest possible extent with the laser pulses operating independently. Figure 1 shows the TOF mass spectra of CS₂ molecules irradiated by both 267-nm and 400-nm laser pulses at a zero delay time (Figure 1(a)), or by only a 267-nm or 400-nm laser pulse (Figure 1(b) and (c)). There were some parent ions (CS₂⁺) detected in the spectra shown in Figure 1(b) and (c), which were produced via multiphoton ionization of the 267-nm or 400-nm laser pulse. The intensity of CS₂⁺ ions was greatly enhanced with both laser pulses overlapped both temporally and spatially, which is shown in Figure 1(a). Fragment ions, S⁺ and CS⁺, can be observed

by employing the pump-probe scheme (Figure 1(a)), but almost no such ions appeared in the mass spectra when using only one laser pulse (Figure 1(b) and (c)). Thus, time dependence of S^+ or CS^+ fragment ions can be recorded by measuring the ion intensity as a function of pump-probe delay time. The ion yield of parent CS_2^+ produced by each laser pulse was small compared with that produced by both laser pulses, and did not change with the pump-probe delay time. Therefore, the time-resolved evolution of parent CS_2^+ ions can also be obtained by subtracting the background signal produced by each laser pulse.

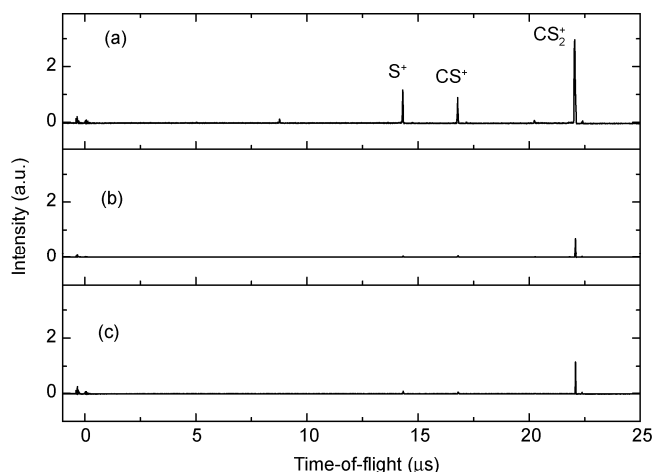


Figure 1 TOF mass spectra of the CS_2 molecules recorded with (a) both 267-nm and 400 nm lasers at zero delay time, (b) 267-nm laser only, and (c) 400-nm laser only.

2.2 Transient pump-probe behavior of different ions

Figure 2(b) shows time dependence of CS_2^+ ions over the delay range -4 ps to $+6$ ps. All pump-probe transients shown in this paper were base-line corrected by subtracting the background signals, and were normalized to the highest intensity point in the pump probe transient. The delay time was positive (negative) if the 400-nm laser pulse followed (preceded) the 267-nm pulse. Time zero of the two laser pulses and the autocorrelation function (or instrumental response) were determined by performing the pump-probe experiment on benzene, and the result is shown in Figure 2(a). The pump-probe transient signal of benzene has a symmetric Gaussian profile, and our instrumental response time had a 260-fs full-width-at-half-maximum (FWHM).

From the transient pump-probe behavior of CS_2^+ , one can see that the ion intensity decayed exponentially for delay times $t > 0$, which can be attributed to the evolution of the electronic excited state pumped by the 267-nm laser pulse. It should be noted that the ion intensity was not zero at $t < 0$. Indeed, as $|t|$ increased, the ion intensity exponentially decayed. Similar phenomena were also observed in the transient pump-probe behavior of the fragment ions, CS^+ and S^+ (see Figure 3). As mentioned above, the delay time $t < 0$ means that the 400-nm laser pulse interacts with CS_2 molecules before the 267-nm laser pulse. Because of relatively high intensity of the 400-nm laser used in this study, it is possible that the CS_2 molecules can be pumped to another electronic state through multi-photon absorption of the 400-nm laser pulse, and probed via ionization by 267-nm laser pulse. Proper fitting of the transient pump-probe

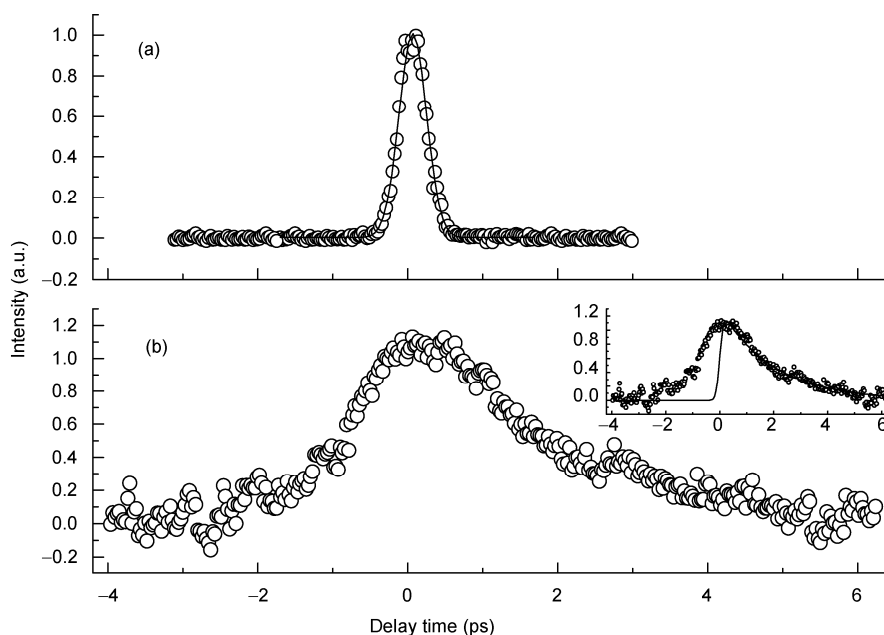


Figure 2 (a) Measurement of the autocorrelation function by pump-probe experiment of benzene. The Gaussian fitting of the transient gives the instrumental response of 260 fs. (b) Time dependence of CS_2^+ signal in the delay time from -4 ps to $+6$ ps. The insert shows the fitting of the CS_2^+ transient using eq. (2), which is not suitable to fit the component at $t < 0$. See text for details.

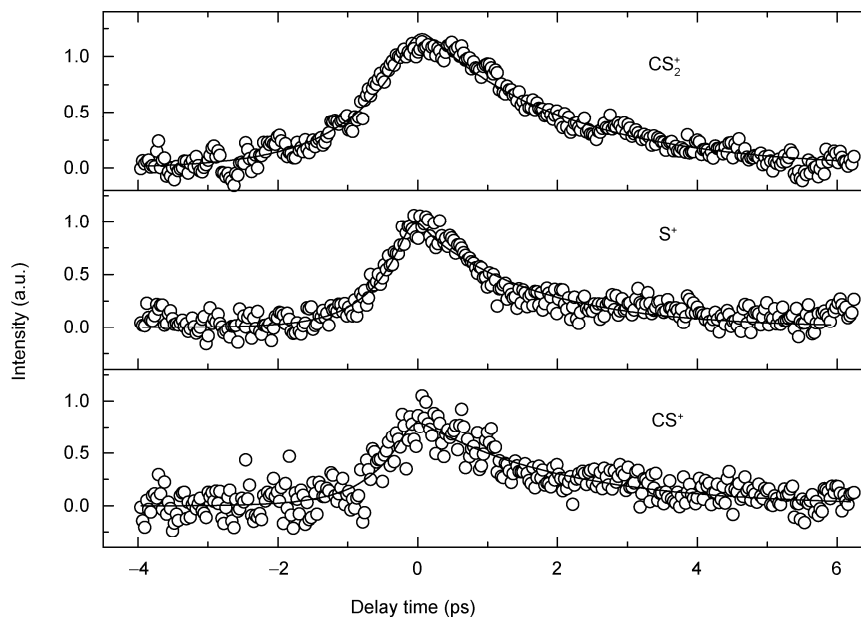


Figure 3 Time dependence of ion signals of parent CS_2^+ , fragment S^+ and CS^+ , and the fitting results using eq. (3).

behavior over the whole range of the delay time allows us to obtain the evolution of the two electronic states pumped by the 400-nm and 267-nm laser pulse simultaneously with one pump-probe experiment.

The femtosecond transients were analyzed using a least-squares fitting program [31]. To account for the instrumental response, the measured time-dependent signal $S(t)$ in this experiment is given by convolution of one exponential decay term with a Gaussian response function $g(\tau)$:

$$S(t) = C_1 \int_{-\infty}^t g(\tau) \exp[(t-\tau)/\tau_1] dt, \quad (1)$$

which can be solved analytically to give

$$S(t) = C_1 \exp\left[\left(\frac{\sigma}{2\tau_1}\right)^2 - \frac{t+t_0}{\tau_1}\right] \left[1 - \text{erf}\left(\frac{\sigma}{2\tau_1} - \frac{t+t_0}{\sigma}\right)\right], \quad (2)$$

where C_1 is the amplitude of the exponential term with decay time τ_1 , t is the delay time between the two laser pulses, and t_0 is a parameter that accounts for slight mismatches of the assigned zero delay times of the experiment. σ is related to the FWHM of the autocorrelation function by $\sigma = \text{FWHM}/1.665 = 156$ fs.

Eq. (2) can be used to fit the component of the transient at $t > 0$. However, it cannot be used to fit the component at $t < 0$, because the value of $S(t)$ according to the equation drops to zero at $t < 0$, which is shown in the insert of Figure 2. To analyze the transient behavior and obtain the lifetimes of different electronic excited states from one best-fit procedure, we modified eq. (2) to be

$$\begin{aligned} S(t) &= S_1(t') + S_2(-t') \\ &= C_1 \exp\left[\left(\frac{\sigma}{2\tau_1}\right)^2 - \frac{t'+t_0}{\tau_1}\right] \\ &\quad \times \left[1 - \text{erf}\left(\frac{\sigma}{2\tau_1} - \frac{t'+t_0}{\sigma}\right)\right] \\ &\quad + C_2 \exp\left[\left(\frac{\sigma}{2\tau_2}\right)^2 - \frac{-(t'+t_0)}{\tau_2}\right] \\ &\quad \times \left[1 - \text{erf}\left(\frac{\sigma}{2\tau_2} - \frac{-(t'+t_0)}{\sigma}\right)\right] (t' > 0). \end{aligned} \quad (3)$$

Thus, the first and the second terms of eq. (3) refer to the components where $t > 0$ and $t < 0$, respectively. Figure 3 shows the transient behavior of parent CS_2^+ ions, fragment S^+ and CS^+ ions, as well as their best fitting results using eq. (3). The decay times, τ_1 (for $t > 0$) and τ_2 (for $t < 0$) of different ions were obtained from the least-squares fitting, and were summarized in Table 1. The transient behavior of the fragment ions (S^+ and CS^+) was similar to that of the parent ions CS_2^+ , which indicates that the fragment ions were produced from dissociation of CS_2^+ ions. From Figure 3 and Table 1, one can see that the decay times were different for $t > 0$ component and $t < 0$ component, indicating that different electronic excited states were involved during the pump step.

At excitation wavelength near 267 nm, the absorption spectrum of CS_2 is void of any features. Thus, a one-photon 267-nm excitation process will not occur. According to the (2+1) REMPI experimental study by Morgan et al. [15],

Table 1 A summary of the lifetimes obtained from the fitting the transient behavior shown in Figure 3

Ion	CS ₂ ⁺	S ⁺	CS ⁺	Process	Intermediate state
<i>t</i> <0 lifetime (fs)	830±30	570±40	670±70	400-nm pump 267-nm probe	[² Π _g]4f Rydberg
<i>t</i> >0 lifetime (fs)	2000±50	1700±70	1900±100	267-nm pump 400-nm probe	6sσ _g (or 4dπ _g) Rydberg

CS₂ molecules can be excited from the ground state ($X^1\Sigma_g^+$) to the vibronic origin of the Rydberg state, $[3/2]6s\sigma_g(^3\Pi_g)$, by two-photon absorption of the 267-nm laser. The decay dynamics of the $[3/2]6s\sigma_g(^3\Pi_g)$ origin has been investigated previously by Liu et al. [25] using femtosecond time-resolved mass spectra of CS₂⁺ with a 400-nm probe. The lifetime was determined to be 1034 fs, and the decay of the CS₂⁺ ion signal was attributed to predissociation of the $[3/2]6s\sigma_g(^3\Pi_g)$ state through intersystem crossing via a repulsive potential surface. The dynamics of a superposition of vibrational excited 6s and 4p Rydberg states were studied later by Knappenberger et al. [26] using femtosecond time-resolved photoelectron spectroscopy. They showed that the decay time exhibits sensitivity to the electronic and vibrational states excited by the pump laser. The lifetime of the $[3/2]6s\sigma_g(^3\Pi_g)$ origin was measured to be 2200 fs, while the lifetimes of the vibrational excited states were as little as 530 fs. In this work, the transient behavior of both the parent ions (CS₂⁺) and fragment ions (CS⁺, S⁺) were observed, and the fragment ions were produced by dissociation of the parent ions. Thus, the final ionic state of the pump-probe scheme should be a dissociative electronic state (probably C state of CS₂⁺ as discussed in the following), which is different from that in the literature. The lifetime τ_1 of the *t*>0 component was measured to be 2000 fs (1700 fs and 1900 fs) by fitting the transient of CS₂⁺ (S⁺ and CS⁺), in reasonable agreement with the picosecond-scale lifetime of the $[3/2]6s\sigma_g(^3\Pi_g)$ origin reported by Knappenberger et al. [21].

Because the bandwidth of the laser is about 220 cm⁻¹, the vibrational states of the 4d Rydberg state will also be excited. Thus, the excited state accessed in the two-267-nm-photon pump step at *t*>0 could be a 6s or 4d Rydberg state.

For the *t*<0 component, the subpicosecond lifetime obtained from fitting the transient behavior of the ions indicated that a different excited state was accessed in the pump step by multi-photon absorption of the 400-nm laser. The CS₂ molecule has a strong absorption band in the 185–230 nm region, which is attributed to the transition from the ground $X^1\Sigma_g^+$ state to the $^1B_2(^1\Sigma_u^+)$ state [14]. At first glance, the excited state accessed in the 400-nm pump step could be assigned to the $^1B_2(^1\Sigma_u^+)$ state by two-photon absorption. However, we excluded this state by the following three reasons. First, the $^1B_2(^1\Sigma_u^+)$ state has an almost constant lifetime of 400 fs around 200 nm [14], which is smaller than the lifetime obtained in the present study. Second, as discussed above, two photons of the 267-nm laser were absorbed in the pump-probe experiment. The total energy of

two 267-nm photons plus two 400-nm photons is 15.49 eV, which is lower than the dissociation limit of CS⁺. However, we observed CS⁺ fragment ions in this study. Third, a direct two-photon $g \rightarrow u$ transition from the $X^1\Sigma_g^+$ state to the $^1B_2(^1\Sigma_u^+)$ state is forbidden. Therefore, a two-photon 400-nm transition to the $^1B_2(^1\Sigma_u^+)$ is unlikely to occur. According to the results of the (3+1) REMPI spectra reported by Morgan et al. [15], peaks in the total excitation energy range 74000–75000 cm⁻¹ were assigned to the three-photon transition from the $X^1\Sigma_g^+$ state to the [²Π_g]4f-Rydberg state. Hence, the time-dependent ion yield at *t*<0 could be attributed to the evolution of the 4f-Rydberg state pumped by a three-400-nm-photon absorption. The lifetime of the 4f-Rydberg state was found to be 830 fs (570 fs and 670 fs) by fitting the transient behavior of CS₂⁺ (S⁺, and CS⁺). In the time-resolved photoelectron measurement studied by Knappenberger et al. [27], the lifetime of the [²Π_g]4f ($^3\Delta_{2u}$) Rydberg state was found to be 760 fs, which is in good agreement with the lifetime reported here.

2.3 Dissociative ionization of CS₂ in the femtosecond pump-probe experiment

In this work, fragment ions (S⁺ and CS⁺) were observed in the pump-probe experiment, allowing us to discuss the ionization/dissociation of CS₂ molecules in the femtosecond laser fields. Both the S⁺ and the CS⁺ signals showed similar time-dependence to the parent ions, and the fitting results gave almost identical lifetimes. The results strongly suggest that the fragment ions were produced from dissociation of the parent ions. As discussed in Section 2.2, five photons were absorbed by CS₂ molecules in our pump-probe experiment, i.e. two 267-nm + three 400-nm photons. The energy of these five photons is 18.59 eV (8.53 eV above the ionization potential of CS₂), which is higher than the appearance potential of S⁺ (14.81 eV), CS⁺ (15.78 eV) or S₂⁺ (16.91 eV). However, the fragment ions observed in the pump-probe experiment were mainly S⁺ and CS⁺, while little S₂⁺ was observed at any delay time. The branching ratio of S⁺/CS⁺ is useful information in the determination of the final ionic excited state and the dissociation dynamics. The C²Σ_g⁺ state of CS₂⁺ is totally predissociative via the repulsive ⁴Σ⁻ state and correlates to the S⁺ + CS and CS⁺ + S product channels. In their photoelectron photoion coincidence (PEPICO) study, Aitchison and Eland [17] found that S⁺ and CS⁺ were produced in 57:43 ratio from the dissociation of the C²Σ_g⁺ state over the energy range of 16.19–16.5

eV. The S^+/CS^+ ratios in the dissociation of the C state were also measured by Hwang et al. [21] in a state-selected study using the optical-optical double resonance technique. They found that the S^+/CS^+ branching ratio was 1.27 for dissociation starting from the vibrational origin of the C state, and almost unitary from dissociation starting from the vibrational excited states. For the states lower than the $C^2\Sigma_g^+$ state, Zhang et al. [19] found that the high vibrational levels of the $B^2\Sigma_u^+$ state can dissociate to produce S^+ and CS^+ as well, and the S^+/CS^+ branching ratio can be as large as 4.0. The main products in the dissociation of the $D^2\Pi_u$ state and other higher energy states are also S^+ and CS^+ . However, the S^+/CS^+ ratio is reversed in comparison with the $C^2\Sigma_g^+$ state [17]. In this study, the branching ratios of S^+/CS^+ were measured as a function of the delay time, which is shown in Figure 4. It was found that the S^+/CS^+ ratio was about 1.5 near “time-zero” (averaged value within ± 150 fs delay time range), in good agreement with the results for the C state in previous studies, which suggests that the final ionic state in the pump-probe experiment is the $C^2\Sigma_g^+$ state of CS_2^+ .

The S^+/CS^+ ratio decreased as the delay time increased. The S^+/CS^+ ratio was around 1.5 at $t = 0$, but it dropped to 0.5 at $t = -1$ ps or $t = +1.5$ ps. This indicates that the $CS^+ + S$ channel was enhanced more than the $S^+ + CS$ channel as the wavepacket evolved along the intermediate Rydberg state. The dissociation dynamics of CS_2^+ in the $C^2\Sigma_g^+$ state were presumed to follow the $C^2\Sigma_g^+ \rightarrow ^4\Sigma^-$ crossing by all previous researchers. Hwang et al. [21] argued that the $C^2\Sigma_g^+ \rightarrow ^4\Sigma^-$ crossing occurs at a larger bending different displacement along the CS^+ production path than that along the S^+ path. We cannot determine the final vibronic state of CS_2^+ with our photo-ion measurements. However, the observed dependence of the S^+/CS^+ ratio on the delay time of the pump and probe lasers indicates that the dissociation process of CS_2^+ is related to the evolution of the Rydberg state. As the wavepacket moves along the Rydberg state, it

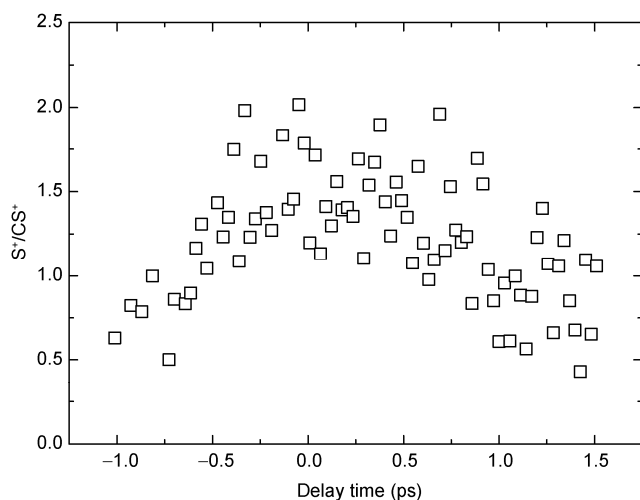


Figure 4 Branching ratio of S^+/CS^+ as a function of delay time.

may be excited to different areas of the potential energy surface of the $CS_2^+ C^2\Sigma_g^+$ state, which is favorable to the CS^+ dissociation channel. It would be helpful to carry out a high-level theoretical calculation of the potential energy surface of CS_2^+ to achieve a more insightful view of the dissociation dynamics related to CS^+ and S^+ production.

3 Conclusion

CS_2 is an interesting prototypical polyatomic system. Because of the rich information about its neutral and ionic states, the initial and final states can be well defined in the pump-probe experiments. In addition, investigation of the dynamics is still of current research interest because of the complicated physical processes in the excited states. In this work, we carried out an ultrafast time-resolved study of this prototype molecules using time-of-flight mass spectroscopy. The transient behavior of both parent ion (CS_2^+) and fragment ions (S^+ and CS^+) were obtained, allowing us to further investigate the ultrafast dynamics and dissociative ionization of CS_2 . All ion signals decay exponentially with different lifetimes for delay time $t > 0$ and $t < 0$. The $[3/2]6s\sigma_g(^3\Pi_g)$ Rydberg state is likely to be pumped by two 267-nm photons at $t > 0$, while at $t < 0$, the $[^2\Pi_g]4f$ Rydberg state may be excited by three-400-nm-photon absorption. The lifetimes of these two Rydberg states were obtained simultaneously from one pump-probe experiment through the fitting of the transient behavior. The similarity of the transient behavior of the fragment ions to that of parent ion indicated that S^+ and CS^+ were produced by dissociation of CS_2^+ . In addition, the final ionic state of CS_2^+ is the $C^2\Sigma_g^+$ state based on the measured S^+/CS^+ branching ratio. The S^+/CS^+ ratio decreases as the delay time between the two lasers increases, which indicates that the dissociation process of CS_2^+ is related to the evolution of the intermediate Rydberg state. Achieving a more insightful view of the dissociation dynamics of CS_2^+ may need a high-level calculation of the potential energy surface of the ionic states.

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