CS$_2$ decay dynamics investigated by two-color femtosecond laser pulses

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The Rydberg-state decay dynamics of carbon disulfide (CS$_2$) has been investigated by $(2+1')$ resonance-enhanced multiphoton ionization with the pump-probe technique (pump wavelength 266 nm and probe wavelength 400 nm) on our homebuilt femtosecond laser system. The CS$_2$ is pumped into Rydberg state $6s\sigma_g$ by two 266-nm photons, corresponding to the excitation energy 9.4 eV, and then ionized by temporally delayed 400-nm pulse. The CS$_2$ ion yield dependence on the time delay determines the excited-state lifetime to be 409 ± 6 fs for C^{32}S^{32}S and 441 ± 7 fs for C^{32}S^{34}S, respectively, at 265 nm pump and the isotopically averaged lifetime 1034 ± 31 fs at 267.5 nm pump. The wavelength dependence of the lifetime may be due to the effect of electron spin on the potential energy surface—namely, separately subjected to two different mechanisms: internal conversion and intersystem crossing interaction.

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I. INTRODUCTION

The dissociation process of small polyatomic molecules excited by a laser pulse at various wavelengths is a subject in current chemistry that has attracted much interest [1–5]. The investigation of dissociation will give a fundamental principle of how the excited molecule evolves into its fragments in the manner of bond breakage due to intramolecular energy flow. The short molecular excited-state lifetime in the UV range often means that there will be an interaction between the bound and repulsive potential energy surfaces where the lifetime dependence on the wavelength will reveal more information on the electronic structure of molecule in greater detail.

Carbon disulfide (CS$_2$), as a prototypical triatomic molecule similar to carbon dioxide (CO$_2$), has been investigated extensively, especially in the vicinity of energy 50 000 cm^{-1} concerning the excited state S_3 $(\tilde{A}$ $^1B_2$ $^1\Sigma_u^+)$ by various methods [1–19]. Its excited-state lifetime at around 200 nm has been determined by many research groups [1–14] by different methods such as absorption linewidth, angular product distribution, resonance Raman depolarization ratios, and time-resolved spectroscopy, where only the pump-probe technique could monitor the photodissociation process in real time while other methods essentially rely on the natural linewidth measurement which introduces many uncertainties in the lifetime estimation. In 1990, Li and Myers [3] measured the depolarization ratios of resonantly excited light emission for low-pressure CS$_2$ vapor at room temperature in three distinct spectral regions on resonance with the intense predissociative S_3-S_0 electronic transition. The analysis of the depolarization dispersion curves gave the J-averaged

excited-state lifetimes varying from 1.5 ps near 212 nm to 0.44 ps near 200 nm. The frequency dependence of the CS$_2$ predissociation lifetime is similar to that obtained over the region from 201 to 216 nm by Hara and Phillips [8] but the absolute lifetime measurement is incomparable with the previous results [9,10] due to different excitation wavelength. Using jet-cooled laser-induced fluorescence and dispersed spectra, Liou et $al.$ [11] studied the $^1B_2$ $^1\Sigma_u^+$ state of CS$_2$ at 210 nm and deduced the lifetime of this state to be 4.4 ps from the transition linewidth. Later, he and other co-operators recorded the jet-cooled rotationally resolved spectra of the predissociation band Σ_0^g of the $^1B_2$ state of CS$_2$ at 210 nm with a technique of stimulated pumping and found that the transition linewidth is predissociation broadened by as large as 1.79 cm^{-1} [16]. For the first time, Baronavski and Owrutsky [6] used femtosecond ultraviolet $1+1$ multiphoton ionization spectroscopy to directly measure the lifetime of state S_3 as 600 ± 100 fs at 205 nm photoexcitation but argued that fluorescence quantum yields method [8] gives a more reliable lifetime wavelength dependence than the absolute measurements. With the assumption that the overall photodissociation process occurs on a time scale of 1.5 ps, Frey and Felder [13] explained this photodissociation rationally at 193 nm. Mank et $al.$ [1] studied the photodissociation dynamics of the $^1B_2$ state of CS$_2$ at the excitation wavelength 214-198 nm giving a lifetime of 2.8 ± 0.3 ps at the rotational temperature of 30 K at 47560 cm^{-1} and 0.3–0.4 ps at 193 nm. Farmanara et $al.$ [2] recently performed a direct measurement of the lifetime of the excited state S_3. The ultrafast predissociation in the CS$_2$ molecule excited by 250-fs femtosecond laser pulses at 194–207 nm reveals that the ion-signal time-dependent lifetime decreases from 620 fs down to 180 fs for tuning the excitation wavelength from 207 nm to 194 nm. A nearly constant plateau at about 200 nm in the energy dependence of the lifetime reflects the barrier of the transition from the bent to a quasilinear geometry of the excited CS$_2$ molecule. After obtaining the $(1+1)$

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resonance-enhanced multiphoton ionization spectra of jet-cooled CS_2 at 220–208 nm, Beatty *et al.* [7] tabulated the predissociation lifetimes for the upper-state 34 vibrational bands.

In the wavelength region around 266 nm, however, no dynamics work has been reported yet except for some spectral work [20–22]. In the present paper, we investigated the photodissociation process of CS_2 by the pump-probe technique in real time and studied the wavelength dependence of the excited-state lifetime. Our 266-nm and 400-nm laser pulses, generated by third harmonics and second harmonics, respectively, served as the pump and probe laser beam separately.

II. EXPERIMENT

Our homebuilt solid-state femtosecond laser system consists mainly of a seed oscillator, a chirped regenerative amplifier containing a stretcher and a compressor, and nonlinear optics. The femtosecond laser seed pulse is generated in an Ar^+ laser (Innova 300, Coherent) pumped self-mode-lock Ti:sapphire oscillator providing 250-mW, 86-MHz, 15–20 fs narrow pulses. The output pulse is temporally stretched to be 150 ps and 200 mW before selectively admitted into a chirped regenerative amplifier cavity pumped by the SHG output of a Q-switched Nd:YAG laser with 5 mJ per pulse at working frequency 3 kHz. The pulse is amplified for several times in the cavity and runs out at the maximum power and then temporally compressed to be $\sim$60 fs, $\sim$600 mW ($\sim$200 μJ per pulse).

The fundamental light is frequency doubled by a β-BaB_2O_4 crystal (BBO, type I) to produce the second harmonic generation (SHG) pulse, centered at about 400 nm. The output of BBO I is separated into SHG and fundamental lines. These two beams are then overlapped spatially and temporally into another BBO crystal (type II) to generate the third harmonic generation (THG). The residual SHG in the BBO II output is then directed into a delay stage (SIGMA KOKI SP26-150, Japan), while the THG light is introduced into time-of-flight mass spectrometer (TOF MS) via f =26 cm quartz plano-convex focus lens and fused silicon window. The time-delayed SHG is also focused by the same focus lens and collinearly aligned with THG into TOF MS. Typical power values of the SHG and THG beams in front of the window are about 20 and 2–3 μJ.

The time-of-flight mass spectrometer used in our experiment is of a typical Wiley-McLaren type. Briefly, the TOF-MS consists of two chambers: a molecular beam source chamber and a flight chamber separately pumped by 500 l/s and 1500 l/s Turbo pumps. The sample gas, continuously injected into the source chamber via a 0.8-mm capillary array (Hamamatsu, J5022-01), directly expands across the ionization-accelerating region. The ionized molecules are extracted and accelerated by a typical three-electrode system and detected by a three-stage microchannel plate (MCP) detector at the end of the TOF-MS. The ion signals are recorded and averaged by a computer-controlled transient digitizer (STR81G, Sonix). With the beam on, the pressures of the source chamber and the electron beam ionization-flight
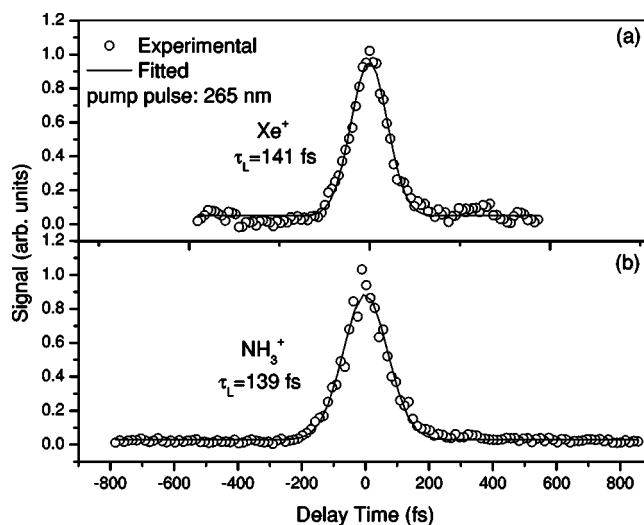

FIG. 1. Pump-probe signal for Xe and for NH_3. The profile fit determines the laser pulse width to be 141 fs for Xe (a) and 139 fs for NH_3 (b), consistent with each other.

chamber are maintained lower than 10^{-3} and 10^{-4} Pa, respectively. A typical TOF mass spectrum is obtained over 5000 laser shots averaging at fixed delay time.

III. RESULTS AND DISCUSSION

The pump-probe experiment is performed first on a well-studied molecule—for example, NH_3 or Xe—in aid of the system calibration from which the instrumental response function (or autocorrelation function) and the zero-delay-time position can be simultaneously obtained. Either of them has a symmetric pump-probe profile indicating that the signal can extract the information of instrumental response and zero-delay-time point accurately. Their pump-probe signals and Gaussian-fitted results are shown in Figs. 1(a) and 1(b), separately, which are well consistent with each other. The determined instrumental response function widths for Xe and NH_3 are $\tau_L=141$ fs and $\tau_L=139$ fs, respectively, at a pump wavelength 265 nm.

Following the calibration, the time-of-flight mass spectrum of CS_2 versus the pump probe delay time is recorded. The TOF mass spectrum of CS_2 has only one strong parent cation peak under our laser power. The other two signals of CS^+ and S^+ are too weak to extract the pump probe signal. The delay time dependence of the pump-probe signal is shown in Fig. 2. Based on a generally simplified model that the observed signal is the convolution of the exponential decay function and the autocorrelation one, the decay lifetime of CS_2 at 265 nm pulse pump can be determined to be $\tau=409\pm6$ fs for $C^{32}S^{32}S$ and $\tau=441\pm7$ fs for $C^{32}S^{34}S$, respectively, while when the pump wavelength is tuned to 267.5 nm, the signal is very weak and only the isotopically averaged lifetime determined with value $\tau=1034\pm31$ fs. Here the instrumental response is taken as $\tau_L=228$ fs for the wavelength change. It can be seen in Figs. 2(a) and 2(b) that the lifetimes of $C^{32}S^{34}S$ and $C^{32}S^{34}S$ at 265 nm are close but
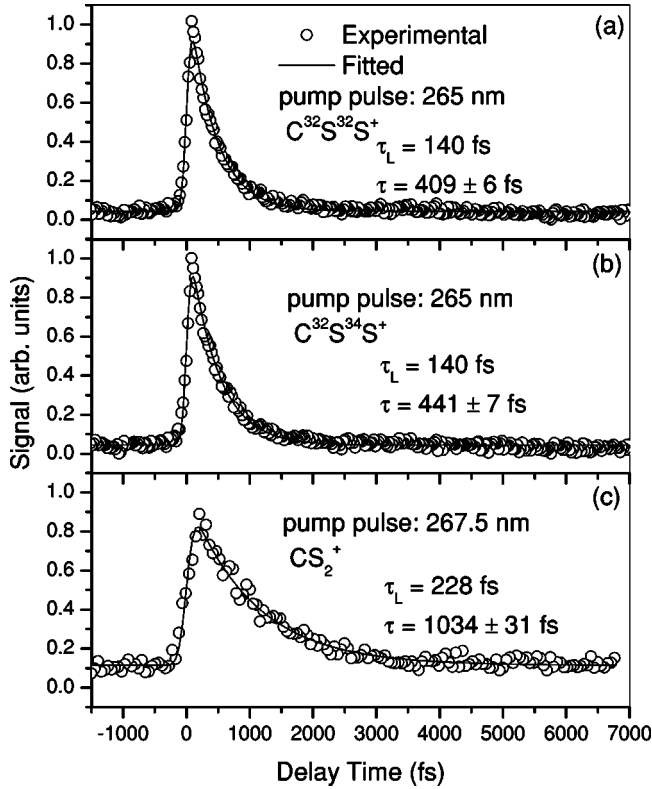
FIG. 2. Pump-probe signal for C^{32}S^{32}S and C^{32}S^{34}S at 265 nm pump and for CS$_2$ at 267.5 nm pump. At 265 nm pump, the lifetimes are determined to be 409±6 fs for C^{32}S^{32}S (a) and 441±7 fs for C^{32}S^{34}S (b), slightly different from each other due to different mass numbers. At 267.5 nm pump, however, the isotopically averaged lifetime is determined to be 1034±31 fs (c), much longer than that at 265 nm pump. At these two different pump wavelengths, the pulse durations are taken as 140 fs and 228 fs separately.

with a discrepancy of about 30 fs due to the different mass number. Figure 2(a), however, shows that the lifetime at 267.5 nm is greatly prolonged by more than 2 times, probably hinting at more profound different dynamics mechanisms.

According to the (2+1) resonantly enhanced multiphonon ionization (REMPI) experimental result of Morgan *et al.* [20] our wide-bandwidth laser ~266 nm ($\Delta\nu_{\mathrm{FWHM}}$=370 cm^{-1}) pumps the ground CS$_2$ into the Rydberg state $6s\sigma_g$ by two-photon absorption. Based on their spectral assignment, the excited states in our experiment are the vibronic origin of Rydberg state $\left[\frac{3}{2}\right]6s\sigma_g{}^3\Pi_g$ at 267.5 nm and state $\left[\frac{1}{2}\right]6s\sigma_g{}^1\Pi_g$ at 265 nm [20], separated by an energy of about 480 cm^{-1}, corresponding to the orbit-spin interaction constant 440 cm^{-1} provided the wide bandwidth considered. At this excitation energy, the dissociation reaction

$$\mathrm{CS}_2 \rightarrow \mathrm{CS}(X\,^1\Sigma^+) + S(^3P), \qquad (1)$$

$$\mathrm{CS}_2 \rightarrow \mathrm{CS}(a\,^3\Pi) + S(^3P) \qquad (2)$$
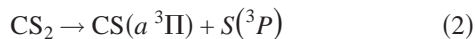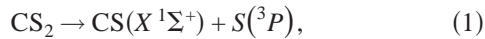
can occur with threshold energies of 4.46 eV and 7.85 eV, respectively, and channel (2) is highly favored as soon as the

energetic threshold ($\lambda \sim 158$ nm) is exceeded [20,23].

The prominent dependence of the lifetime on the pump wavelength is interesting. When the pump wavelength varied from 265 nm to 267.5 nm, the lifetime became longer, which is similar to the wavelength dependence of the lifetime at ~200 nm pump [1–5,8]. In the work of Farmanara *et al.* [2] the determined lifetime decreases from 620 fs down to 180 fs for tuning excitation wavelength from 207 nm to 194 nm with an average tuning rate ~34 fs/nm and they found a nearly constant lifetime plateau at about 200 nm. In our experiment, however, the lifetime is strongly dependent on the pump wavelength, varying from about 420 fs at 265 nm to 1 ps at 267.5 nm with a tuning rate ~240 fs/nm, far larger than that at 200 nm. Farmanara *et al.* [24] determined the lifetime of CS$_2$ at one 155-nm photon pump to be about 1.9 ps. But we cannot make sure if there will exist a similar constant plateau in the wavelength range between 155 and 130 nm for lack of knowledge on the lifetimes at other wavelengths. The large discrepancy of lifetimes can also be deduced from the spectral observation presented in Ref. [2], where the component $\left[\frac{3}{2}\right]6s\sigma_g{}^3\Pi_g$ has a sharper structure than $\left[\frac{1}{2}\right]6s\sigma_g{}^1\Pi_g$, implying a longer lifetime. It also manifests the former is less predissociated than the latter. Wu [25] presented a collinear model to explain the predissociation of CS$_2$ at 130.4 nm that a repulsive potential curve is proposed to be responsible for the dissociative excitation of CS$_2$. As we have known, however, the CS$_2$ ground state is $\widetilde{X}\,^1\Sigma_g^+$ with spin number 0, so the state $\left[\frac{1}{2}\right]6s\sigma_g{}^1\Pi_g$ will most probably dissociate through internal conversion (IC) and $\left[\frac{3}{2}\right]6s\sigma_g{}^3\Pi_g$ through the intersystem crossing (ISC) via the repulsive potential surface. In the latter case, the dissociation is usually slow, but it will accelerate with the increasing of the intersystem crossing interaction. Since the $\left[\frac{3}{2}\right]6s\sigma_g{}^3\Pi_g$ state has a picosecond-scale lifetime, the ISC interaction may be strong enough to correspond to the weaker spectral line in our experiment.

IV. CONCLUSION

Using the pump-probe (2+1′) resonantly enhanced multiphoton ionization spectroscopy with two-color femtosecond laser pulses, we have directly observed the photodissociation of CS$_2$ in real time at ~266 nm excitation. The dissociation lifetimes are determined to be 409±6 fs for C^{32}S^{32}S and 441±7 fs for C^{32}S^{34}S at 265 nm pump and 1034±31 fs at 267.5 nm pump. The lifetime discrepancy is explained by the internal conversion and the intersystem crossing interaction, respectively.

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