

Dynamics of excited OCS investigated by resonance-enhanced multiphoton ionization

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(Received 7 November 2001; published 19 April 2002)

The predissociation decay behavior of molecule carbonyl sulfide (OCS) has been investigated by resonance-enhanced multiphoton ionization spectroscopy using the pump-probe technique of dichroic femtosecond lasers in real time. The lifetime of excited OCS around $74\,720\text{ cm}^{-1}$ by two-photon absorption of 268 nm, corresponding to $v_1 = 1$ of the Rydberg state $[^2\Pi_{1/2}]4p\pi(^1\Sigma^+)$, is directly determined to be $\tau_D = 1071 \pm 11$ fs. This picosecond decay process indicates that the excited state is predissociative. The temporal information of dissociation enriches the knowledge of the potential-energy surface of the associative excited state.

DOI: 10.1103/PhysRevA.65.052503

PACS number(s): 33.70.Ca, 33.80.Rv, 33.80.Gj, 82.53.Eb

I. INTRODUCTION

The dissociation process of small polyatomic molecules excited by laser pulse at various wavelengths is an attracting subject in current chemistry [1,2]. The investigation of the dissociation will give a fundamental principle of how the excited molecules evolve into its fragments in the manner of bond breakage due to the intramolecular energy transfer. This energy flow from the reactants to the products can be described by nuclear motion on the potential-energy surface (PES). Contrarily the natural and easy way to gain an insight into the PES of the excited molecules is to investigate the photodissociation events, for example, to measure the transitional and internal energy distribution of the dissociation products, or the spectral homogeneous-broadening containing the dissociation temporal information or the population density variation of the reactant and product versus the reaction evolution time [3–5]. The experiments to determine dissociation lifetime can be classified as direct and indirect. As for the latter, however, there may exist many factors to affect the observed variables, e.g., the linewidth-broadening in spectra, resulting in the fact that the determined lifetimes of the same state by different apparatus, even by the same apparatus but under different experimental environments, e.g., jet expansion conditions, are often contrary. With the recent advent of ultrashort-pulse laser technology [6], a complementary experimental means, pump-probe technique, has been invented and applied to investigate the ultrafast phenomena in a more direct way [1]. This pump-probe technology requires two laser beams, one for exciting the sample molecule into the concerned state and the other for probing the excited state or fragment products after a time delay. The time delay dependence of products' population reflects the photodissociation process in real time. This method has been applied to a variety of molecules and molecular complexes and has proved to be a promising technique to study the transition state dynamics in real time. The products' population can be investigated by many methods [3–5] such as simple absorption, stimulated-emission pumping, laser-

induced fluorescence, or photofragment ionization. In our experiment, the resonance-enhanced multiphoton ionization (REMPI) and time-of-flight mass spectrometer (TOF MS) is additionally employed to monitor the density variation of interested states and to identify the various species with different mass-to-charge ratio, respectively. However, the spectra of different vibrational states, even different electronic states of the same species can not be distinguished in TOF MS for its low resolution, and the attribution of determined lifetime often needs the information of the corresponding photospectrum of the researched species at the same wavelength. In most cases, the determined lifetime by this method is often rotationally, even vibrationally averaged.

Carbonyl sulfide (OCS), with other sulfur-containing pollutants such as CS_2 , H_2S , has attracted many researchers in the past two decades for its worldwide distribution [7–11]. As a prototypical triatomic molecule with symmetry $C_{\infty v}$ in the ground state, OCS has an abundant spectrum in the microwave, infrared, UV, and VUV (visible ultraviolet) range [3,12–24]. The spectra in the later wavelength range are concerned with a certain electronically excited state and the characteristic feature in spectra often encodes some information of the molecular structure, e.g., the PES avoiding crossing, to some extent. Hishikawa *et al.* [12] investigated the femtosecond photodissociation dynamics of OCS on the dissociative PES of the electronically excited $^1\Sigma^+$ state by photofragment excitation (PHOFEX) spectroscopy and found the vibrational motion at the transition state with a period of 42 fs. Pibel *et al.* [13] recorded the PHOFEX spectrum near 154 nm with a resolution of better than 1 cm^{-1} . By measuring the homogeneous line broadening, an estimate for this excited-state's lifetime is given as $\tau > 0.26$ ps. In their other work [3,14], the homogeneous broadening of the dissociative state is determined as 37 cm^{-1} , corresponding to a lifetime of 0.14 ps. Later, Ohde *et al.* [15] measured the broadening of the same dissociative state at several transition peaks with lifetime 50 fs at 152.6 nm, 31 fs at 150.6 nm, and 140 fs at 154.5 nm determined. The speed and angular distribution of final product from the photodissociation of OCS have also been measured by many authors [13,14,25–36].

In this paper, we report our pump-probe experiment on OCS and measure the lifetime of OCS at two 268-nm photon excited Rydberg state $[^2\Pi_{1/2}]4p\pi(^1\Sigma^+)$. The population

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density of the excited state is monitored by the delayed 402-nm pulse through multiphoton ionization. The ion signal dependence on the variation of the time delay will reflect the OCS dissociation process in real time.

II. EXPERIMENT

Our homebuilt femtosecond laser system has been introduced in previous work [37]. Briefly, it consists mainly of a seed oscillator and a chirped regenerative amplifier with a stretcher and compressor. The 803-nm femtosecond laser pulse is generated in an Ar⁺ laser (Innova 300, Coherent) pumped Ti:sapphire oscillator. The pulse out from this self-mode-locked oscillator, with 15–20 fs duration, 250 mW average power, and 86-MHz repetition rate, is temporally stretched and then amplified by a chirped regenerative amplifier pumped by the SHG (second-harmonic generation) output of a Q-switched Nd:YAG (yttrium aluminum garnet) laser with 5 mJ per pulse at working frequency 3 kHz. At the last step the amplified pulse is compressed back to ~60 fs with bandwidth ~24 nm. Its maximum power can exceed ~700 mW (~250 μJ per pulse). The central wavelength and bandwidth of the fundamental pulse are measured by the monochromator (Jarrell-Ash, Division of Fisher Scientific Co., U.S.A.).

The time-of-flight (TOF) mass spectrometer used in our experiment is a typical Wiley-McLaren-type one. The sample gas, continuously injected via a capillary array (Hamamatsu, 0.8 mm with 12 μm diameter for each), directly passes into the ionization-accelerating region. The ions in this region are extracted and accelerated by a typical three electrodes system. After a zero-field-free flight of about 35 cm, the ions are detected by a two-stage microchannel plate (MCP) detector at the end of the flight tube. The detected signal is recorded by a transient digitizer (STR 81G, Sonix), inserted in a desktop computer. With beam on, the pressures of the source chamber and flight chamber are maintained at lower than 10⁻³ and 10⁻⁴ Pa, respectively.

The pump and probe pulses are produced by second-harmonic and third-harmonic generation (THG) of the fundamental 803-nm pulse. The blue light, centered at 402 nm, is the frequency-doubled output of the 803 nm by a BBO crystal (type I, SHG), and then temporally and spatially recombined into another BBO crystal (type II, THG) with the residual fundamental pulse from the SHG BBO to produce the third-harmonic output, centered at 268 nm. The residual 402-nm light from the THG BBO output is directed onto a computer-controlled optical delay stage to provide a delay-time-variable pulse, relative to the 268-nm one.

The 268-nm and 402-nm light are collinearly focused, by a quartz plano-convex lens with 30-cm focal length, into the intersection area in the TOF mass spectrometer through a Brewster window. Both beams propagate perpendicular to the flight axis and their polarization is arranged to be parallel to the detector. The maximum powers of 268-nm and 402-nm lights are about 3 μJ and 20 μJ, respectively.

A typical TOF mass spectrum is obtained over 3000 laser shots' averaging at fixed delay time. The pump-probe decay curve is averaged over several delay-time scans at the same

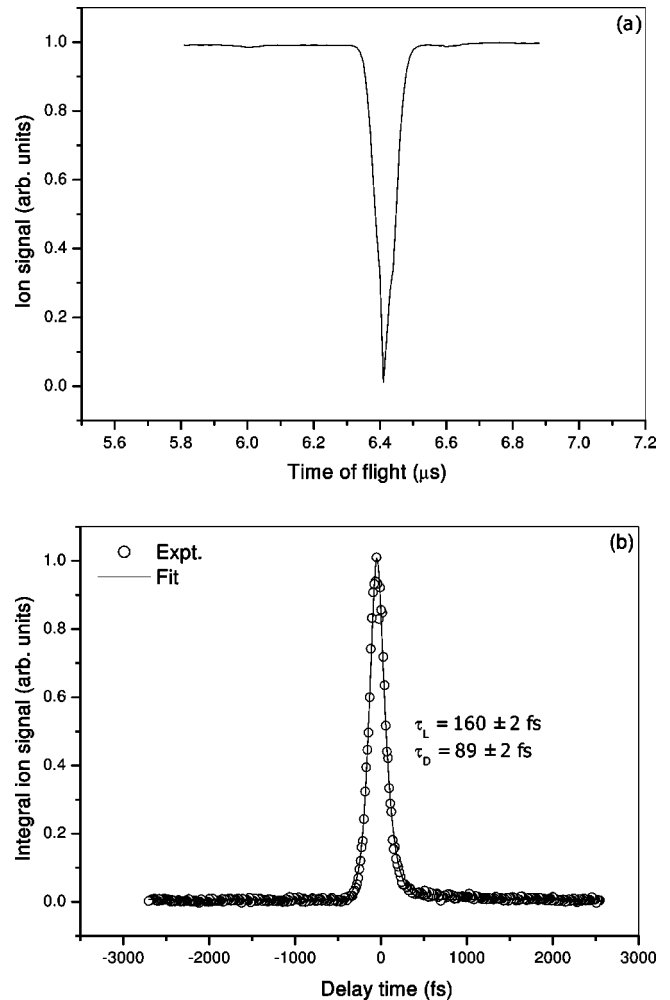


FIG. 1. (a) Typical time-of-flight mass spectrum of NH₃ in pump probe. (b) The pump-probe delay time dependence of the integral ion signal for NH₃.

chamber pressure. The stagnation pressure of the sample gas is guaranteed by carefully controlling the inlet valve connecting the ionization chamber and the large gas buffer with pressure about 20 kPa.

III. RESULT AND DISCUSSION

The pump-probe experiment is performed first on an over-researched molecule, for example, NH₃ for the system calibration. A typical time-of-flight mass spectrum of NH₃ is shown in Fig. 1(a) and its delay-time dependence in Fig. 1(b). The observed short single exponential decay signal is the convolution of the exponential decay function $F(t)$ and the instrumental response function $G(t)$ [38,39]:

$$I_{obs}(t) = \iint F(t-t_1)G(t-t_2)dt_1dt_2\delta(t-t_1-t_2), \quad (1)$$

where the instrumental response function of this technique is the cross-correlation function of the pump and probe pulse

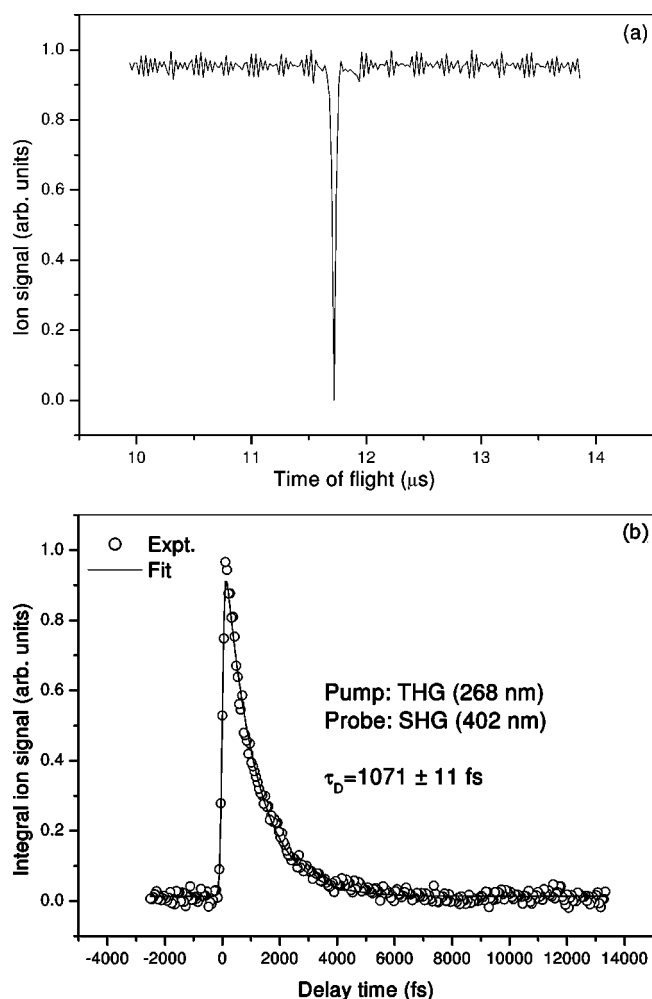


FIG. 2. (a) Typical time-of-flight mass spectrum of OCS in pump probe. (b) The pump-probe delay time dependence of the integral ion signal for OCS.

that has a $\text{sec}^2(t)$ or Gaussian profile. In our case, the Gaussian function is employed for convenience to simplify the data disposal. A nonlinear least-squares fit can be performed to our experimental data based on the model of Eq. (1). The fit line is also drawn in Fig. 1(b), which is in excellent coincidence with the circled experimental data. The instrument responding function width and dissociation lifetime are determined as $\tau_L = 160 \pm 2$ fs and $\tau_D = 89 \pm 2$ fs, respectively. The zero delay-time point is also determined in the fit. Due to very short dissociation time $\tau_D = 89 \pm 2$ fs, the determined cross-correlation width τ_L and zero delay-time point with NH_3 will have a high accuracy and reliability.

The typical TOF mass spectrum of OCS is shown in Fig. 2(a) and the integral OCS⁺ signal's dependence on delay time in Fig. 2(b) with circle points. The TOF mass spectrum has an obvious peak of the parent ion. When the probe laser power varies strongly, the ion signal of fragment S⁺ comes to appear although it is very weak. No CO⁺ fragment ion was observed in our experiment. It is difficult to extract pump-probe signal for fragment S⁺ from TOF spectra due to its weakness, we mainly monitored the deexcitation process

of the OCS⁺ signal. The decay profile in Fig. 2(b) presents the single exponential decay dissociation process in real time. Based on the same model of Eq. (1) and with the determined instrumental responding function width and zero delay-time point, the lifetime of OCS is determined as $\tau_D = 1071 \pm 11$ fs. The fit line is also drawn in Fig. 2(b), agreeing with the circled experimental data well.

In fact, we can determine the instrumental response function width, the decay lifetime constant, and the zero time-delay point simultaneously by the least-squares fit to the OCS experimental data without any calibration. It gives the response function width 166 ± 5 fs, very near 160 ± 2 fs determined by the calibration molecule NH_3 , and the decay lifetime 1068 ± 11 fs, in line with 1071 ± 11 fs obtained with the aid of NH_3 calibration, which further affirms the rationality of the numerical results. This coincidence also implies that no excitation occurs at 402-nm pump since the same single exponential decay modal is employed in both cases.

Our observed lifetime is attributable to the Rydberg state $[^2\Pi_{1/2}]4p\pi(^1\Sigma^+)v_1=1$. Morgan *et al.* [16] recorded the $(2+1)$ REMPI spectrum within $70\,500\text{--}86\,000\text{ cm}^{-1}$ and assigned unambiguously the line peak at $74\,814\text{ cm}^{-1}$ as $[^2\Pi_{1/2}]4p\pi(^1\Sigma^+)1_0^1$. In our experiment, at 268-nm photoexcitation, the ground state OCS can arrive at the Rydberg state around $2h\nu = 74\,720\text{ cm}^{-1}$, deviating from $74\,814\text{ cm}^{-1}$ by 94 cm^{-1} , but it is covered by the full width at half maximum energy range ($74\,534\text{--}74\,906\text{ cm}^{-1}$). In this range no other states are populated in abundance, limited by the transition selection rule; thus the determined lifetime would be attributable to the $v_1=1$ Rydberg state.

As there are no other measurements for the lifetime at this wavelength excitation, the direct contrast is inaccessible. However, we can make an indirect comparison with the aid of the spectral information. In Refs. [16–19] the spectrum covering $71\,500\text{--}75\,000\text{ cm}^{-1}$ with the spectral linewidths having nearly the same value was recorded, indicating that the excited states at this wavelength region have lifetimes in the same order. This lifetime feature may be mainly due to the fact that all lines here are attributable to the same electronic transition upper state $[^2\Pi]4p\lambda(\lambda=\sigma,\pi)$. This spectral feature is very different from the diffuse bands with wider linewidth around 154 nm concerning transition $^1\Sigma^+ - \bar{X}^1\Sigma^+$. At 154.5-nm ($64\,740\text{ cm}^{-1}$) excitation, Yamanouchi and co-workers [3,14] and Ohde *et al.* [15] deduced the dissociation lifetime to be 0.14 ps with a line broadening $\Delta\nu = 37\text{ cm}^{-1}$ and Pibel *et al.* [13] determined it to be $\tau > 0.26$ ps with line broadening $\Delta\nu = 20\text{ cm}^{-1}$. In order to get the lifetime information at our energy excitation, we can compare the spectral linewidth at these two wavelength ranges. McCarthy and Vaida [20] recorded the jet-cooled absorption spectrum in the range of $62\,000\text{--}72\,000\text{ cm}^{-1}$, making it possible to compare the lifetime at the same experimental condition, and found that the spectral linewidth around $64\,740\text{ cm}^{-1}$ is 4–6 times broader than that around $71\,787\text{ cm}^{-1}$, implying that the corresponding lifetime in the former range is 4–6 times shorter than that at the later range, namely, the lifetime in our

case is 0.56–0.84 ps or 1.04–1.56 ps, in line with our result, 1071 ± 11 fs, determined by pump-probe method. This picosecond lifetime predissociation indicates an intersection between the bound potential surface and the repulsive one, similar to CS₂ at the same excitation wavelength [40].

The weakness of fragment spectra can be simply explained by the energy coincidence. The work of Black *et al.* [21] shows that the OCS molecule predissociates when excited in the energy range of around 267 nm and that the main dissociation products are the S atom and CO ($\tilde{X}^1\Sigma^+$). The ionization of ground-state sulfur atom requires 10.36 eV and the *S* state sulfur atom requires 7.61 eV, so at least three 402-nm photons are needed to produce S⁺, which implies a great weak ionization signal of S⁺, in good coincidence with our experimental observation. Having a higher ionization potential of about 14 eV [41], as CO is concerned, it requires at least five 402-nm photons to ionize. This process does not occur in our experiment due to the weakness of the 402-nm pulse.

IV. CONCLUSION

Using the pump-probe resonance-enhanced multiphoton ionization spectroscopy with dichroic femtosecond laser pulses, we have directly observed the photodissociation of OCS at double 268-nm excitation in real time. The dissociation is determined to occur in about 1 ps, characterized by lifetime 1071 ± 11 fs. The excited state selected by the double 268-nm photons is $[^2\Pi_{1/2}]4p\pi(^1\Sigma^+)v_1=1$, which can be further verified by our forthcoming REMPI photoelectron energy spectrum.

ACKNOWLEDGMENTS

This work was supported by NKBRFSF and the NSFC Foundation (Nos. 29833080, 20003012, and 29973044), and by the Chinese Postdoctoral Sciences Foundation.

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