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$\tilde{A}\,^2\Pi_u$ state-intermediated two-photon dissociation of CS_2^+ via the first channel

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The $[1+1]\,\tilde{A}\,^2\Pi_u$-state resonance enhanced two-photon dissociation process of CS_2^+ molecular ions has been investigated by measuring the photofragment S^+ excitation (PHOFEX) spectrum in the wavelength range of 424–482 nm, where the CS_2^+ molecular ions were prepared purely by $[3+1]$ multiphoton ionization of the neutral CS_2 molecules at 483.2 nm. The PHOFEX spectrum was assigned essentially to the $CS_2^+(\tilde{A}\,^2\Pi_u)\leftarrow CS_2^+(\tilde{X}\,^2\Pi_g)$ transition, and the dissociation mechanism of CS_2^+ was preliminarily attributed to (i) $CS_2^+(\tilde{X}\,^2\Pi_g)\rightarrow CS_2^+(\tilde{A}\,^2\Pi_u)$ through one-photon excitation, (ii) $CS_2^+(\tilde{A}\,^2\Pi_u)\rightarrow CS_2^+(\tilde{X}^\dagger)$ via internal conversion process due to the vibronic coupling between the $\tilde{A}$ and $\tilde{X}$ states, (iii) $CS_2^+(\tilde{X}^\dagger)\rightarrow CS_2^+(\tilde{B}\,^2\Sigma_u^+)$ through the second photon excitation, and (iv) $CS_2^+(\tilde{B}\,^2\Sigma_u^+)\rightarrow S^+ + CS$ owing to the potential curve crossing with the repulsive $^4\Sigma^-$ state correlated with the first dissociation limit. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1377600]

I. INTRODUCTION

Photodissociation of molecules lies at the heart of spectroscopy and photochemistry. Besides its practical importance, experimental studies of molecular photodissociation often provide useful information on the intra- and intermolecular dynamics or, more specifically, the curve crossing, interference, spin–orbit coupling between the electronic states, the energy transfer from one mode to the others, and the breaking of bonds to form fragment products, etc.[1,2] The development of sophisticated new experimental methods, often involving several lasers, has made it possible to study the fragmentation mechanism in unprecedented precision. From such experiments one can derive information concerning the excitation mechanism, the internal energy transfer within the excited complex, and the actual bond rupture.

In this work, we investigated the photodissociation study of CS_2^+ ions through two-photon resonant excitation. Previously many investigators had studied experimentally the spectrum and the dissociation dynamics of CS_2^+.[3–23] Laird and Barrow[3] first observed the CS_2^+ emission in the ultraviolet (UV) range. This emission system was studied at higher resolution by Callomon,[4] who confirmed the spectral assignment and showed by the rotational analysis that it involves transitions between the doubly degenerate $\tilde{X}\,^2\Pi_g$ and the excited $\tilde{B}\,^2\Sigma_u^+$ states. A second visible emission system was observed by Leach[5] and assigned to an $\tilde{A}\,^2\Pi_u\rightarrow\tilde{X}\,^2\Pi_g$ transition. Both transition systems were subsequently studied by several other investigators using various excitation sources to generate the electronically excited CS_2^+ ions, such as photoionization,[6–11] electron impact,[12–15] Penning ionization,[16,17] and charge transfer.[18,19] These works show clearly that all the three electronic states of CS_2^+ ion are bound states and the geometries are linear with the C–S bond lengths being 1.5542, 1.615, and 1.5641 Å in the $\tilde{X}\,^2\Pi_g$, $\tilde{A}\,^2\Pi_u$, and $\tilde{B}\,^2\Sigma_u^+$ states, respectively,[4,13] and that both in the ground $\tilde{X}\,^2\Pi_g$ state and the excited $\tilde{A}\,^2\Pi_u$ state there exist strong Fermi resonances between vibrational levels involving the symmetric stretch ν_1 and overtones of the bending vibration ν_2. In addition to these three bound electronic states, the higher excited state, named as $\tilde{C}\,^2\Sigma_g^+$, was observed from the photoelectron spectroscopy,[6–8] and studied further by Frey *et al.*[10] and Wang *et al.*[11] to determine the vibrational frequencies. The $\tilde{C}\,^2\Sigma_g^+$ state was found to be fully predissociative and correlated with both $S^+ + CS$ and $S + CS^+$ fragments.[20] Momigny *et al.*[12] proposed a model to account for the metastable levels in CS_2^+ leading to $S^+(^4S)+CS(X\,^1\Sigma^+)$ and $CS^+(X\,^2\Pi)+S(^3P)$ under electron impact on CS_2 molecules, in which the curve crossing from the $\tilde{C}\,^2\Sigma_g^+$ state to a fully repulsive $^4\Sigma^-$ or/and a repulsive $^2\Sigma^-$ state should be responsible for the predissociation. The dissociation dynamics in the $\tilde{C}\,^2\Sigma_g^+$ state was studied in detail by Maier and co-workers[21,22] and recently by Hwang *et al.*[23] using two-color optical–optical double resonance method. These works had determined the predissociative lifetimes and the CS^+/S^+ branching ratios, as well as the average kinetic energy releases for several vibrational levels in the $\tilde{C}$ state.

Despite of many works on the spectrum of CS_2^+ in the $\tilde{X}$, $\tilde{A}$, and $\tilde{B}$ states and the dissociation dynamics in the $\tilde{C}$ state, there has been no report about the photodissociation of CS_2^+

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in the states below the $\tilde{C}$ state. According to the model proposed by Momigny *et al.*,[12] the $^4\Sigma^-$ repulsive state, which correlates with the first dissociation limit $\mathrm{S}^+(^4\mathrm{S})+\mathrm{CS}(\mathrm{X}\,^1\Sigma^+)$, also crosses the $\tilde{X}\,^2\Pi_g$, $\tilde{A}\,^2\Pi_u$ and $\tilde{B}\,^2\Sigma_u^+$ states at their highly excited vibrational levels. If this is really the case, CS_2^+ cations lying at high vibrational levels in the $\tilde{B}\,^2\Sigma_u^+$ state should be predissociative. However, due to the narrow Franck–Condon contour for the $\tilde{B}\,^2\Sigma_u^+-\tilde{X}\,^2\Pi_g$ transition,[13] direct excitation from the ground state $\tilde{X}\,^2\Pi_g$ to the high vibrational levels in the $\tilde{B}$ state is improbable. Therefore, an intermediate state is necessary to pump through to the high vibrational levels in the $\tilde{B}$ state. In this report, we prepared the CS_2^+ ions cleanly by $[3+1]$ REMPI through the $4p$ Rydberg state at 483.2 nm,[24,25] and excited the CS_2^+ ions to vibrationally excited levels in the $\tilde{B}$ state from the $\tilde{X}$ state by $[1+1]$ two-photon resonant excitation via intermediate bound state $\tilde{A}\,^2\Pi_u$. Only S^+ fragment ions were observed in the energy region of this study. The excitation and dissociation processes to form S^+ fragments were investigated through the S^+ excitation spectrum.

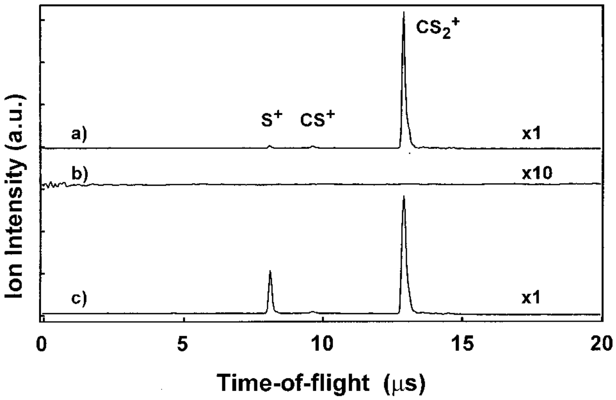

FIG. 1. The TOF mass spectra averaged over 256 laser shots and obtained with (a) only the photoionization laser at 483.2 nm, (b) only the photodissociation laser at 460.6 nm, and (c) both the photoionization laser and the dissociation laser overlapped spatially and temporally with each other. The CS_2^+ ions in (a) and (c) were generated via $[3+1]$REMPI of CS_2 molecules by the ionization laser, and the S^+ ions in (c) were produced from the dissociation of CS_2^+ ions by the dissociation laser. The pulse energies of the ionization laser and the dissociation laser were optimized and maintained at 2 and 1 mJ, respectively.

II. EXPERIMENT

The present experimental setup consists of (i) a pulsed molecular beam source to generate the jet-cooled CS_2 molecules, (ii) two dye laser systems pumped independently by two Nd:yttrium–aluminum–garnet (YAG) lasers, and (iii) a home-made time-of-flight (TOF) mass spectrometer.

The jet-cooled CS_2 molecules were produced by the supersonic expansion of a CS_2/He gas mixture (CS_2/He $\sim 5\%$) through a pulsed nozzle (General Valve) with a nozzle orifice diameter of 0.5 mm into a main chamber. The main chamber was pumped by a turbomolecular pump (1500 1/s) which was backed up by a mechanical pump (70 1/s). The supersonic jet was collimated by a skimmer (3 mm ϕ) located 10 mm downstream from the nozzle orifice, and introduced into the laser-molecule interaction region, which was differentially pumped by a turbo-molecular pump (1500 1/s) with a mechanical pump (15 1/s). The distance between the skimmer and the laser-molecule interaction point is 14 cm. The stagnation pressure was kept at around 1 atm, and the operating pressures in the main chamber and the interaction region were 4×10^{-6} and 4×10^{-7} Torr, respectively.

Two pulsed dye lasers (Lumonics, HD-500), which were pumped independently by the THG (354.7 nm) outputs of two Nd:YAG lasers (Spectra-Physics, GCR-170 and LAB-170), were employed in this experiment. The output of one dye laser, $\sim$2 mJ/pulse, was used as the light source to prepare CS_2^+ molecular ions via $[3+1]$ REMPI of CS_2 molecules. This photoionization laser was focused perpendicularly on the molecular beam of CS_2 by a quartz lens with $f=300\,\mathrm{mm}$, and its wavelength was fixed at 483.2 nm, which corresponds to the three-photon resonance Rydberg transition of $\mathrm{CS}_2,4p\sigma^3\Pi_u\leftarrow X\,^1\Sigma_g^+$. The output of the other dye laser, $\sim$1 mJ/pulse, was employed as the photodissociation light to dissociate CS_2^+ ions via $[1+1]$ excitation. This light was coaxially counterpropagated with the photoionization laser, and focused by another quartz lens with $f=600\,\mathrm{mm}$. Its wavelength was scanned over 424–482 nm to excite the CS_2^+ ions from the ground state to the interest energy region through two-photon excitation. Both dye lasers were temporally and spatially overlapped with each other at the laser-molecule interaction point.

The produced ions, including the parent CS_2^+ ions and the fragment ions, were extracted and accelerated into a TOF mass spectrometer and drifted along a 23 cm long TOF tube, and finally detected by a microchannel plate (MCP) detector. The signals from the MCP output were amplified with a preamplifier (NF, BX-31), and the mass-resolved data were collected by averaging the amplified signals for selected mass species with boxcar averagers (Stanford SR250), and interfaced to a PC for data storage. The intensities of the ionization laser and the photodissociation laser were monitored simultaneously during the experiment.

III. RESULTS AND DISCUSSION

A. Overall TOF mass spectral features

Figure 1(a) shows the TOF mass spectrum obtained with the ionization laser only, by fixing the wavelength at $\lambda=483.2\,\mathrm{nm}$ and maintaining the pulse energy at $\sim$2 mJ. The $[3+1]$ REMPI of CS_2 in this wavelength range had been studied in detail by Baker *et al.*[24] The wavelength of 483.2 nm used in this study corresponds to the single narrow band in the $[3+1]$ REMPI spectrum, which can be expressed as

$$\mathrm{CS}_2(\tilde{X}\,^1\Sigma_g^+)\xrightarrow{3h\nu}\mathrm{CS}_2(4p\sigma\,^3\Pi_u)\xrightarrow{h\nu}\mathrm{CS}_2^+(\tilde{X}\,^2\Pi_g)+e. \tag{1}$$

It is clearly seen in the mass spectrum that the CS_2^+ molecular ions are the predominate products formed at this wavelength, and the amounts of S^+ and CS^+ ions are less than 1% of CS_2^+ ions. As stated by Baker *et al.*,[24] the S^+ and CS^+ ions come from the dissociation of CS_2^+ ions, i.e., the $\mathrm{CS}_2^+(\tilde{X}\,^2\Pi_g)$ ions after being initially formed in the $[3+1]$

REMPI process can absorb nonresonantly two or three photons in succession, and reach to the first or second dissociation limit, and finally yield the fragments $S^+(^4S)$ and $CS(X\,^1\Sigma^+)$, or $CS^+(X\,^2\Pi)$ and $S(^3P)$. This means that we can achieve the soft ionization using the present ionization scheme of [3+1] REMPI. Despite the mechanism in detail, we could certainly prepare exclusive CS_2^+ ions in the $\tilde{X}\,^2\Pi_g$ state with minimum amount of S^+ and CS^+ ions by using a lens with middle focus length ($f=300$ mm) and optimizing the pulse energy of the ionization laser at ~2 mJ.

With the elimination of any obvious interference from the background ions, the photodissociation mechanism of CS_2^+ ions can be investigated by introducing the photodissociation laser. By carefully controlling the intensity of the dissociation laser, no ion signal could be observed only with this laser, as shown in Fig. 1(b) at $\lambda=460.6$ nm. Figure 1(c) shows the action TOF mass spectrum with both the photoionization laser and the dissociation laser, which were overlapped spatially and temporally with each other. It can be seen from the spectrum that remarkably strong S^+ signal appears with the addition of the dissociation laser. The S^+ ions were confirmed to be generated completely from the interaction of the dissociation laser on the parent CS_2^+ molecular ions, by cutting off each of the two lasers, and by varying the temporal delay and the spatial overlap between the two lasers. The power dependence of S^+ signal on the dissociation laser was measured, and showed that S^+ signal intensity depends linearly on the power of dissociation laser. Since the one-photon excitation energy can not access to the dissociation limit of CS_2^+ from its electronic ground state,[12] this power-dependence measurement indicated that the S^+ ions were formed as a result of [1+1] two-photon excitation of the parent CS_2^+ ions by the dissociation laser, i.e., excitation from the electronic ground state to an intermediate state and then to a dissociative state. A scan of the dissociation laser while monitoring S^+ ions enabled us to obtain a photofragment excitation (PHOFEX) spectrum, which contains information related with the two sequential transitions. Therefore, the spectroscopic information on the intermediate state, as well as the dissociation mechanism, can be obtained from the spectrum.

B. Photofragment excitation spectrum

Figure 2 shows the PHOFEX spectrum measured in the wavelength range of 424–482 nm. In the entire scan region no CS^+ ion was observed. With the aid of the spectroscopic data obtained from previous studies on emission spectroscopy of CS_2^+,[4,9,10,13] this PHOFEX spectrum could be assigned completely as the radiative electronic transition, $CS_2^+(\tilde{A}\,^2\Pi_u)\leftarrow CS_2^+(\tilde{X}\,^2\Pi_g)$. This means that the intermediate state in the [1+1] dissociation process to generate S^+ is the $\tilde{A}\,^2\Pi_u$ state of CS_2^+.

As indicated in Fig. 2, the observed resonance peaks in the spectrum correspond to transitions from the (0,0,0) vibrational levels in the $\tilde{X}\,^2\Pi_{g,3/2}$ and $\tilde{X}\,^2\Pi_{g,1/2}$ states to the $v=0-4$ vibrational levels in the $\tilde{A}\,^2\Pi_{u,3/2}$ and $\tilde{A}\,^2\Pi_{u,1/2}$ states, where v represents a group of vibrational levels coupled through Fermi resonance interaction and is defined as $v=v_1+v_2/2$, here v_1 and v_2 denote vibrational quantum numbers for the ν_1 (symmetric stretch) and ν_2 (bend) modes, respectively. Previously, Morgan *et al.*[26] measured the photoelectron spectrum of CS_2 following [3+1] excitation at 483.1 nm, and showed that the populated vibrational levels of CS_2^+ are the (0,0,0) levels in the $\tilde{X}\,^2\Pi_{g,3/2}$ and $\tilde{X}\,^2\Pi_{g,1/2}$ states. This is consistent with our observation, and supports the assignments of our PHOFEX spectrum. Since the resolution of the light source employed in this work (~0.07 cm^{-1}) was higher than those in previous works, more precise spectroscopic constants would be expected. The spectroscopic data analysis is now in progress, and the results will be published in the future.

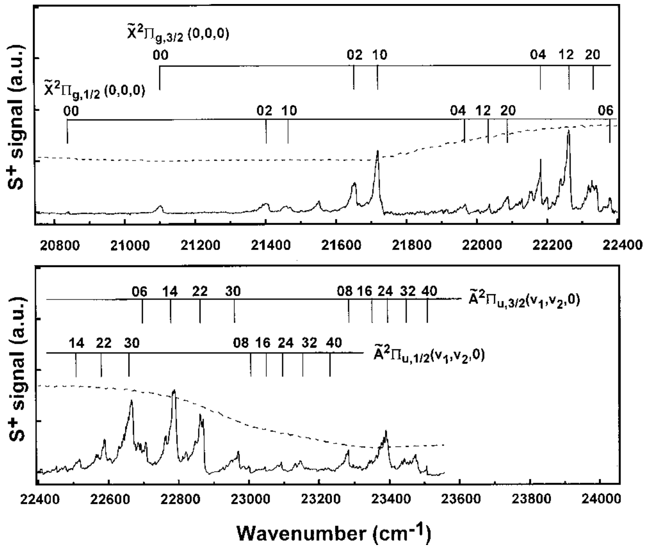

FIG. 2. The PHOFEX spectrum obtained by monitoring S^+ ions in the wavelength range of 424–482 nm. The spectrum was assigned to two series of $\tilde{A}\,^2\Pi_{u,3/2}(v_1,v_2,0)\leftarrow\tilde{X}\,^2\Pi_{g,3/2}(0,0,0)$ and $\tilde{A}\,^2\Pi_{u,1/2}(v_1,v_2,0)\leftarrow\tilde{X}\,^2\Pi_{g,1/2}(0,0,0)$ vibronic transitions of CS_2^+, indicating that the S^+ ions were generated from the $\tilde{A}$ state-intermediated two-photon dissociation process of parent CS_2^+ ions by the dissociation laser. The spectrum is a composite, obtained by splicing together spectra recorded using a number of different dyes, and was not corrected for the laser energy. The dashed curve represents the laser energy variation of the dissociation laser, with respect to the base line of the PHOFEX spectrum.

It is very interesting to notice from Fig. 2 that the $\tilde{A}\,^2\Pi_{u,3/2}(0,0,0)\leftarrow\tilde{X}\,^2\Pi_{g,3/2}(0,0,0)$ and $\tilde{A}\,^2\Pi_{u,1/2}(0,0,0)\leftarrow\tilde{X}\,^2\Pi_{g,1/2}(0,0,0)$ transitions have the weakest intensities among their corresponding transition progressions, i.e., $\tilde{A}\,^2\Pi_{u,3/2}(v_1,0,0)(v_1=0-4)\leftarrow\tilde{X}\,^2\Pi_{g,3/2}(0,0,0)$ and $\tilde{A}\,^2\Pi_{u,1/2}(v_1,0,0)(v_1=0-4)\leftarrow\tilde{X}\,^2\Pi_{g,1/2}(0,0,0)$. This cannot be explained by their Franck–Condon factors, since for a transition between two linear states of similar geometry, $\Delta v_1=v_1'-v_1''=0$ transition should have the strongest intensity. The reason is concerned with the multiphoton excitation and dissociation mechanism of CS_2^+, and will be discussed in the following section.

C. [1+1] photodissociation mechanism

Since the PHOFEX spectrum indicates that the first excitation step in the [1+1] dissociation process to generate

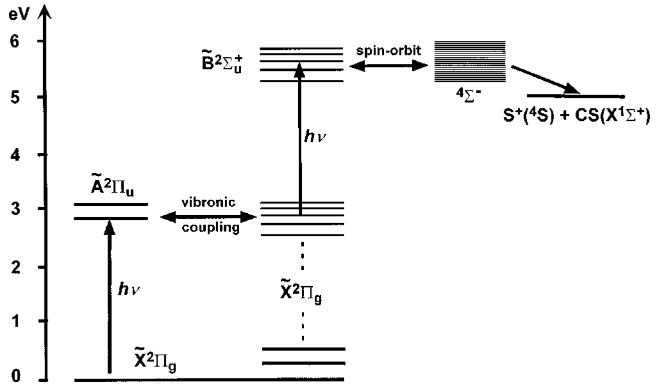

FIG. 3. Schematic energy level diagram of CS_2^+ modified from Refs. 12, 13, and 21 with possible interactions among the electronic states to illustrate the $[1+1]$ excitation and dissociation processes.

S^+ fragments is the $CS_2^+(\tilde{A}\,^2\Pi_u) \leftarrow CS_2^+(\tilde{X}\,^2\Pi_g)$ transition, only the second excitation step is left to be discussed using the present data and those in previous works. Figure 3 shows schematically the relevant energy levels of CS_2^+ modified from Refs. 12, 13, and 21. The first $(S^+ + CS)$ and second $(S + CS^+)$ dissociation limits, both connected with the repulsive $^4\Sigma^-$ state, lie respectively at about 5.0 eV (40 327 cm^{-1}) and 6.0 eV (48 400 cm^{-1}) higher above the vibrationless ground state of CS_2^+.[12] Since the two-photon excitation energy in Fig. 2 varies from 41 500 to 47 100 cm^{-1}, the parent $CS_2^+(\tilde{X})$ ions in this experiment can be energetically excited by two photons to an energy region between the first and second dissociation limits, and dissociate through the $^4\Sigma^-$ state to form S^+ fragments without CS^+ fragments. This is in agreement with the observation that only S^+ fragments exist in the excitation energy range in Fig. 2.

However, direct excitation from the $\tilde{A}\,^2\Pi_u$ state to the $^4\Sigma^-$ state is spin forbidden in the Hund's case (a) approximation, unless the $^4\Sigma^-$ state gains intensity via the spin–orbit interaction which mixes the $^4\Sigma^-$ state and a spin-allowed electronic state. As known from Refs. 13 and 21, the $\tilde{B}\,^2\Sigma_u^+(0,0,0)$ and $\tilde{C}\,^2\Sigma_g^+(0,0,0)$ levels locate respectively at 35 460 cm^{-1} (4.4 eV) and 49 282 cm^{-1} (6.1 eV) higher above the $\tilde{X}\,^2\Pi_{g,3/2}(0,0,0)$ level of CS_2^+. Therefore, the present two-photon excitation cannot energetically reach the $\tilde{C}\,^2\Sigma_g^+$ state, but can reach the energy region of high vibrational levels in the $\tilde{B}\,^2\Sigma_u^+$ state. In this energy region the $^4\Sigma^-$ state may couple with the spin-allowed $\tilde{B}\,^2\Sigma_u^+$ state, and hence, gain some doublet character.

The question is now how the parent CS_2^+ can be excited to the $\tilde{B}\,^2\Sigma_u^+$ state from the $\tilde{A}\,^2\Pi_u$ state. Obviously an electronic transition from the $\tilde{A}\,^2\Pi_u$ state of CS_2^+ to the linear excited state $\tilde{B}\,^2\Pi_u^+$ is strongly forbidden in a one-photon excitation by electric dipole selection rule. One plausible explanation is to consider the possibility of vibronic coupling. There are two possible ways for a forbidden electronic transition to gain intensity: by Herzberg–Teller intensity stealing, which imply a breakdown of the Franck–Condon approximation, or by a breakdown of the Born–Oppenheimer approximation. The vibronic state can only mix with an allowed electronic state of the same symmetry and the extent of the interaction is dependent on the separation of the two electronic states. For the $\tilde{B}\,^2\Sigma_u^+$ state, there does not exist any possible electronic state to mix with via vibronic interaction, whereas for the $\tilde{A}\,^2\Pi_u$ state there exists the high vibrational levels of the $\tilde{X}\,^2\Pi_g$ state nearby to couple with.[12] Therefore, intensity in this forbidden $\tilde{B}\,^2\Sigma_u^+ \leftarrow \tilde{A}\,^2\Pi_u$ transition comes from the vibronic coupling by the $\nu_3(\Sigma_u^+)$ stretching vibration.

According to the earlier considerations, the $[1+1]$ photodissociation process of CS_2^+ in present study may be shown in Fig. 3, and is expressed as

$$CS_2^+(\tilde{X}\,^2\Pi_g) \overset{h\nu}{\rightarrow} CS_2^+(\tilde{A}\,^2\Pi_u), \tag{2}$$

$$CS_2^+(\tilde{A}\,^2\Pi_u) \xleftrightarrow{\text{vibronic interaction}} CS_2^+(\tilde{X}\,^2\Pi_g)^\dagger \tag{3}$$

$$CS_2^+(\tilde{X}\,^2\Pi_g)^\dagger \overset{h\nu}{\rightarrow} CS_2^+(\tilde{B}\,^2\Sigma_u^+)^\dagger \tag{4}$$

$$CS_2^+(\tilde{B}\,^2\Sigma_u^+)^\dagger \xleftrightarrow{\text{spin–orbit}} CS_2^+(^4\Sigma^-), \tag{5}$$

$$CS_2^+(^4\Sigma^-) \rightarrow S^+(^4S) + CS(X\,^1\Sigma^+), \tag{6}$$

where † represents high vibrational levels in the corresponding electronic states.

Now the observation that the S^+ signal is unusually weak for the $\tilde{A}\,^2\Pi_{u,3/2}(0,0,0) \leftarrow \tilde{X}\,^2\Pi_{g,3/2}(0,0,0)$ and $\tilde{A}\,^2\Pi_{u,1/2}(0,0,0) \leftarrow \tilde{X}\,^2\Pi_{g,1/2}(0,0,0)$ transitions in the PHOFEX spectrum can be interpreted with the earlier excitation-dissociation processes. This is not due to the small Franck–Condon factor in the first excitation step, but due to the low efficiency for the second excitation step, since the coupling strength between $\tilde{A}(0,0,0)$ and $\tilde{X}^\dagger$ should be weak owing to the unfavorable overlap of the wave functions in the two states. Whereas for the transitions from $\tilde{X}\,^2\Pi_g(0,0,0)$ to $\tilde{A}\,^2\Pi_u(v_1,0,0)(v_1 = 1-4)$, although the Franck–Condon factor decreases with increasing v_1, the efficiency for the second excitation step, which depends on the wavefunction overlap between $\tilde{A}(v_1,0,0)$ and $\tilde{X}^\dagger$, increases with v_1. Therefore, the combined efficiency for the two sequential excitation steps to produce S^+ ions does not change obviously with v_1.

This excitation-dissociation mechanism was further confirmed by exciting the CS_2^+ ions with a UV light, instead of the visible light. The UV light was the frequency-doubled output of the photodissociation laser employed to record the PHOFEX spectrum in Fig. 2, and tuned in the wavelength region of 212–241 nm. Energetically S^+ ions were expected to exist with this one-photon excitation from the $\tilde{X}\,^2\Pi_g$ state to the $\tilde{B}\,^2\Sigma_u^+$ state. Unfortunately any trace of S^+ ion was not observed in the whole wavelength region. This should be due to the small Franck–Condon factor for the $CS_2^+(\tilde{X}\,^2\Pi_g) \overset{h\nu}{\rightarrow} CS_2^+(\tilde{B}\,^2\Sigma_u^+)^\dagger$ transition, or in other words, the small overlap of the wave functions in the two states, whereas in the case of $[1+1]$ excitation scheme the vibronic coupling between the intermediate $\tilde{A}$ state and the $\tilde{X}$ state enhances the excitation efficiency to the $\tilde{B}$ state, and hence enhances the generation of S^+ fragment ions.

IV. SUMMARY

The $[1+1]$ photodissociation process of CS_2^+ ion was investigated by the S^+PHOFEX spectrum in the wavelength region of 424–482 nm, where the CS_2^+ ions were prepared purely by $[3+1]$REMPI of CS_2 at 483.2 nm. The PHOFEX spectrum was assigned completely as the $CS_2^+(\tilde{A}\,^2\Pi_u) \leftarrow CS_2^+(\tilde{X}\,^2\Pi_g)$ transition, and the S^+ ions were attributed to come from the dissociation of CS_2^+ via the first dissociation limit connected with the repulsive $^4\Sigma^-$ state. The excitation and dissociation process was proposed as (i) resonant excitation from the ground $\tilde{X}\,^2\Pi_g$ state to the $\tilde{A}\,^2\Pi_u$ state, (ii) vibronic coupling which mixes the populated vibrational levels in the $\tilde{A}\,^2\Pi_u$ state and the high vibrational levels in the $\tilde{X}\,^2\Pi_g$ state, and (iii) further excitation from the mixing vibronic levels to the $\tilde{B}\,^2\Sigma_u^+$ state and dissociation via the $^4\Sigma^-$ state through spin–orbit interaction between the $\tilde{B}\,^2\Sigma_u^+$ state and the $^4\Sigma^-$ state. The vibronic coupling between the $\tilde{A}$ state and the $\tilde{X}$ state enhances the efficiency of the second excitation step. It would be interesting to confirm and investigate the $\tilde{A}/\tilde{X}$ coupling by laser-induced fluorescence measurement, and to study in detail the dissociation mechanism at high vibrational levels in the $\tilde{B}$ state. Experiments are now going on along these lines.

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