Photodissociation Dynamics of CS$_2$ Near 204 nm: The S($^3P_J$)+CS($X^1\Sigma^+$) Channels

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We study the photodissociation dynamics of CS$_2$ in the ultraviolet region using the time-sliced velocity map ion imaging technique. The S($^3P_J$)+CS($X^1\Sigma^+$) product channels were observed and identified at four wavelengths of 201.36, 203.10, 204.85 and 206.61 nm. In the measured images of S($^3P_{J=2,1,0}$), the vibrational states of the CS($X^1\Sigma^+$) co-products were partially resolved and the vibrational state distributions were determined. Moreover, the product total kinetic energy releases and the anisotropic parameters were derived. The relatively small anisotropic parameter values indicate that the S($^3P_{J=2,1,0}$)+CS($X^1\Sigma^+$) channels are very likely formed via the indirect predissociation process of CS$_2$. The study of the S($^3P_{J=2,1,0}$)+CS($X^1\Sigma^+$) channels, which come from the spin-orbit coupling dissociation process of CS$_2$, shows that nonadiabatic process plays a role in the ultraviolet photodissociation of CS$_2$.

Key words: Carbon disulfide, Time-sliced velocity map ion imaging, Photodissociation

I. INTRODUCTION

Carbon disulfide (CS$_2$) is a trace component of stratosphere and troposphere, which plays an important role in astrochemistry research [1]. CS$_2$ molecules are the important precursor in the atmospheric sulfur cycle [2–6]. The photodissociation process in the atmosphere is a main sink of CS$_2$ [7–9]. Radicals generated during this process actively participate in various chemical reactions [10–12]. As a result, a number of investigations were performed by researchers into the photodissociation dynamics of CS$_2$ both experimentally [13–17] and theoretically [18–21].

There are extensive literatures on the ultraviolet absorption spectrum of CS$_2$ in the wavelength region from 185 nm to 230 nm [16, 22–25]. This corresponds to a parallel transition from the linear ground state of CS$_2$...
to its \(1\Sigma^+_u \left(^1B_2\right)\) excited state [26]. According to the one-dimensional cuts of the electronic states of linear CS\(_2\) by Trabelsi et al. [18], both \(3\Pi_u\) and \(3\Sigma^-_u\) states correlate to the \(S(3\Pi_J)+CS(X,^1\Sigma^+\,\text{asymptote})\) state.

The photodissociation of CS\(_2\) following excitation to the \(1\Sigma^+_u \left(^1B_2\right)\) state has received considerable academic interests. Previous work mainly focused on the characterization of dynamical information about CS and S fragments. In 1999, Farmanara et al. studied the ultrafast predissociation dynamics of CS\(_2\) molecules with excitation wavelengths from 207 nm to 194 nm using pump-probe experiments [13]. The ultrashort lifetimes for the excited CS\(_2\) molecule were determined and the predissociation dynamics in the \(1\Sigma^+_u \left(^1B_2\right)\) excited state were characterized with high precision. In 2008, the photodissociation dynamics between 208 nm and 217 nm has been investigated by Hu et al. by using a time-of-flight mass spectrometer combined with velocity imaging detection [26]. The (1+1) REMPI spectra of CS\(_2\) were characterized, information about predissociation lifetimes for each vibrational band of \(^1B_2\) intermediate state was determined. By using the sliced imaging technique, Kitsopoulos et al. [28] measured velocity distributions of \(S(3P_{2,1,0})\) and \(S(1D_2)\) photofragments at 193 nm and determined the \(S(3P_{2,1,0})/S(1D_2)\) branching ratios. The spatial anisotropy parameters were obtained from the S-atom angular distributions. In 2004, the dissociation of CS\(_2\) at the same 193 nm was investigated by means of product state-selective vacuum ultraviolet laser ionization using VUV lasers at different wavelengths [22]. Ion images with respect to the \(S(3P_{2,1,0})\) and \(S(1D_2)\) channels were obtained. Besides, it was indicated that these channels are preferentially populated at different geometries by analysis of the obtained anisotropy parameters.

Recently, experimental advances have been made in molecular photodissociation in the vacuum ultraviolet (VUV) region, this is largely due to the development of four wave mixing (FWM) method. The scheme of using the VUV radiation beam combined with the time-sliced velocity map imaging technique has been applied into photodissociation investigation in the VUV region. Preliminary results of the photodissociation study of the N\(_2\)O [29], OCS [30], DNCO [31] molecules as well as the crossed molecular beams study [32] have been presented, in which the VUV detection has also been proven to be a powerful method. In this paper, we report a high-resolution experimental study of the photodissociation dynamic of CS\(_2\) at the photolysis wavelengths from 201.36 nm to 206.61 nm. Using a tunable VUV light source as the detection laser beam in this experiment, the speed and angular distributions of the photolysis products with high resolution have been acquired. The CS\((X,^1\Sigma^+)+S(3P_{J=2,10})\) dissociation channels are clearly identified, where the vibrational states of co-products CS are partially resolved in measured images. This study is beneficial in understanding the nonadiabatic photodissociation mechanisms of CS\(_2\).

II. EXPERIMENTS

The experimental apparatus [33–37] of the present velocity map imaging (VMI) experiments has been shown in detail previously [29, 38–41]. In brief, a molecular beam of 0.3% CS\(_2\) seeded in He was expanded through a pulsed valve (General Valve) with a 0.5 mm diameter nozzle. The pulsed valve was operated at 10 Hz and the stagnation pressure was 800 Torr. The resulting super-sonic molecular beam is propagated upward through a 1 mm diameter skimmer for collimation before reaching the reaction center. The CS\(_2\)/He beam was crossed perpendicularly with the photolysis and probe laser light in the detection chamber.

The photolysis laser beam (\(\sim 204\) nm) was generated by tripling the laser output of a tunable Dye Laser (Sirah, PESC-G-24, Dye Laser 1), which was pumped by a Nd:YAG laser (Spectra Physics PRO-200, Nd:YAG laser 1). The polarization direction of the photolysis laser is set to be parallel to the plane of the imaging detector. A \(\sim 212.55\) nm (\(\omega_1\)) laser beam was generated by doubling the output of a second Dye Laser (Sirah, PESC-G-24, Dye Laser 2), which was pumped by the 355 nm output of a second Nd:YAG laser (Continuum Powerlite9030, Nd:YAG laser 2). A visible laser light at the wavelength around 575 nm (\(\omega_2\)) is generated by the third Dye Laser (Sirah, PESC-G-18, Dye Laser 3), which is pumped by the 532 nm output of the same Nd:YAG laser. In the experiment, \(\omega_1\) and \(\omega_2\) laser beams overlap in space and time, and their focal points are located in the center of the stainless-steel mixing cell. A VUV laser beam at (\(2\omega_1-\omega_2\)) was generated by the four-wave mixing process of pure Krypton gas. The 212.5 nm (\(\omega_1\)) laser beam can also photolyze CS\(_2\) molecules and cause large background. Therefore, the three laser beams are dispersed using a MgF\(_2\) lens according to their different refractive indexes. As a result,
only the VUV laser beam can reach the reaction center and the background signals caused by UV ($\omega_1$) laser beam were eliminated.

The CS($X^1\Sigma^+$)+S($^3P_{J=2,10}$) channels were probed by $(1+1')$ resonance enhanced multiphoton ionization scheme. A visible laser light, serving as the second photon to ionize the S atom products, was generated by the fourth Dye Laser (Sirah, PESC-G-18, Dye Laser 4) pumped by the 532 nm output of the Nd:YAG laser 2 (Continuum Powerlite9030). The photodissociation and ionization of the CS$_2$ molecule occurs in the middle of the second and third electrode of the ion optics. The resulting sulfur ions were accelerated in the electric field formed by the ion optics [34]. It was detected after passing through a 740 mm long time-of-flight tube. The ion detection system is composed of a position-sensitive microchannel plates (MCP) coupled to a phosphor screen (P43). Photons emitted from the phosphor were imaged to a charge-coupled device (CCD) camera (UI-3260CP-M-GL Rev. 2, IDS). The resulting signal was then transferred to the computer and event counting [42] was performed on the obtained images.

In the experiment, a fast 15 ns gate pulse was applied to acquire the time slicing of the product’s new sphere. Two multichannel digital delay generators (DG645, SRS) were used to control the time sequence of each part acting on the reaction center. The wavelength of the $\omega_3$ laser beam was scanned over the Doppler frequency shift, achieving uniform detection of the $S$ fragments with different velocities.

In the detection of $S(^3P_J)$ fragments, the wavelengths of $\omega_3$ were set to 570.98 nm for $S(^3P_0)$, 576.818 nm for $S(^3P_1)$, 575.692 nm for $S(^3P_2)$. 

III. RESULTS AND DISCUSSION

The time-sliced ion images of the $S(^3P_{J=2,1,0})$ products were measured at four photolysis wavelengths of 201.36, 203.10, 204.85, and 206.61 nm, respectively. In the experiment, the energy of the photolysis laser was adjusted to decrease the background signal to a negligible level and optimize the signal-to-noise ratio.

FIG. 1 displays the raw images of $S(^3P_{J=2,1,0})$ products obtained at the wavelength of 201.36 nm. The red vertical arrow in FIG. 1 stands for the polarization direction of the photolysis laser. Those concentric rings observed in the image correspond to the vibrational states of the CS products, and they were partially resolved. It was observed that the $S(^3P_{J=2})$ has a much higher signal intensity in the inner part of the image, compared with the other two levels ($S(^3P_{J=1})$ and $S(^3P_{J=0})$). Concerned with angular distributions of the product, it appears to be more anisotropic with the increase of the ring radius.

A. Product total kinetic energy releases

Through the angular integration of a certain radius in the obtained raw images, the velocity distribution of the product could be obtained. The product total kinetic energy release (TKER) in the center-of-mass frame is converted from the velocity distribution through conservations of momentum and energy. The kinetic energy distributions contain information about the internal energy distribution of the diatomic co-fragment CS products. Considering the energy distribution of the whole system, the TKERs can be expressed by the following equation:

$$\text{TKER} = E_{hv} - D_0 (\text{CS} - \text{S}) - E_{\text{int}} (\text{CS}) - E_{\text{int}} (\text{S})$$ (1)

Here $E_{hv}$ represents the photon energy of photolysis laser, $D_0 (\text{CS} - \text{S})$ denotes the bond energy of the C–S bond, which has been determined by previous studies, $E_{\text{int}} (\text{CS})$ is the internal energy of CS products, and the $E_{\text{int}} (\text{S})$ is the energy difference between the S atom products and the ground state $S(^3P_2)$.

The TKER spectra of the CS$_2$ following the photodissociation at 201.36 nm are shown in FIG. 2. The open circles represent the experimental data and the red solid curves superimposed on it represent the global results of a multiplet fitting. The green solid curves are used to fit the original experimental data, and each peak can be assigned to the vibrational states of the CS co-products. The energy differences between the adjacent rotational states of CS products are too small to resolve...
FIG. 2 Total kinetic energy release distributions (TKERs) for the \( \text{CS}(X^1\Sigma^+)+S^{(3P_{J=2,1,0})} \) channels from the photodissociation of \( \text{CS}_2 \) at 201.36 nm. Results for all \( J \) levels of the sulfur atom products are shown. In each plot, peaks are assigned to the vibrational states of the correlated CS products.

in the experimental images. Therefore, the detailed information on the rotational state distributions was not derived. The energy combs on the upper part of TKERs curves correspond to the center position of the fitting peak. The deviation between the attribution result and the vibrational peak in the TKERs is believed to be caused by the vibrational excited \( \text{CS}_2 \) molecules. For the \( S^{(3P_2)} \) and \( S^{(3P_1)} \) channels, CS products populate as high as \( v=11 \), and the highest vibrational population state for \( S^{(3P_0)} \) is \( v=10 \). It was noted that the general features of TKERs for the three \( ^3P_J \) spin-orbit channels are somewhat different from each other. For \( S^{(3P_2)} \) channel, the intensities increase gradually with the increase of the vibrationally quantum number, and reach its maximum value at \( v=10 \), then decrease rapidly. For \( S^{(3P_0)} \) and \( S^{(3P_1)} \) channels, the intensities have a maximum at \( v=7 \) or \( v=8 \), respectively.

FIG. 3 Anisotropy parameters for individual vibrational states in \( S^{(3P_{J=2,1,0})}+\text{CS}(X^1\Sigma^+) \) channels at four different photolysis wavelengths.

B. Product angular distribution

The angular distributions \( I(\theta) \) of different products in a photodissociation process could be obtained by integrating the three-dimensional spatial distribution over a proper range of speed using the following equation:

\[
I(\theta) = \left(\frac{1}{4\pi}\right) (1 + \beta P_2(\cos\theta))
\]

where \( \beta \) is the spatial anisotropy parameters, \( \theta \) represents the angle between the polarization axis of the photolysis laser and the recoil velocity of the product, and \( P_2(\cos\theta)=1/2(3\cos^2\theta-1) \) is the second order Legendre polynomial. Correspondingly, the \( \beta \) values of each vibrational state were determined. The measured \( \beta \) values for each vibrational state of CS at the four photolysis wavelengths are shown in FIG. 3. It is found that the functions of \( \beta \) values change with the CS vibrational quantum numbers, following similar trends at different wavelengths. That is, it increases from small positive values from \( v=0 \), reaches the maximum value at \( v=1 \) or
$v=2$, and then decreases gradually.

The $\beta$ values at those relatively low CS vibrational states show an obvious difference at different photolysis wavelengths, with the increase of CS vibration quantum numbers, the values obtained at different wavelengths tend to be similar. The $\beta$ values are all small positive values, indicating that the photolysis products mainly come from the indirect predissociation process of CS$_2$.

C. Product branching ratios

From the fitting method mentioned above, the relative vibrational state populations of the correlated CS products were derived and are displayed in FIG. 4. The function of the branching ratios with the vibrational quantum numbers was similar at different photolysis wavelengths for the same $J$ level.

It can be observed that the CS vibrational distributions of the $S(^3P_2)$ channel are a little different from that of $S(^3P_0)$ and $S(^3P_1)$. The branching ratios of the low and high vibrational state of CS in the $J=0$ and $J=1$ channels are relatively smaller, the products mainly populate in the middle region ($v=4, 5, 6, 7$). In contrast, the $S(^3P_2)$ products distribute more in high vibrational states. With the increase of the vibration quantum numbers, the branching ratio increases gradually, reaching a maximum value at $v=9, 10$, and then decreases rapidly. Because the detection efficiency is different for the three $J$ levels of $S(^3P_J)$ products, the relative branching ratios among different $J$ components are not presented.

CS$_2$ has a linear structure at its ground electronic state $X^1\Sigma_g^+$ and belongs to the $D_{\infty h}$ point group [43, 44]. The ground electronic state electron configuration is $(\text{core})(5\sigma_g)^2(4\sigma_u)^2(6\sigma_g)^2(5\sigma_u)^2(2\pi_u)^4(2\pi_g)^4$ [24]. A finely structured potential energy surface is required in order to obtain detailed information about the photodissociation dynamics. According to the potential energy surfaces derived by Francisco et al. [18], the photon excitation energies around 204 nm correspond to the excitation to the linear $^1\Sigma_g^+$ electronically excited states. The potential of this $^1\Sigma_g^+$ state is characterized to be flat and shallow. It is noted that two triplet states correlate adiabatically with the present triplet dissociation channel. That is, the $^3\Sigma_g^-$ state correlates to the $S(^3P_J)+CS(X^1\Sigma^+)$ dissociation limit at relatively large CS distances. Besides, the repulsive state $^3\Pi_g$ also correlates with the $S(^3P_J)+CS(X^1\Sigma^+)$ asymptote. This suggests that the product $S(^3P_J)+CS(X^1\Sigma^+)$ observed in this study should be formed via spin-orbit coupling of $^1\Sigma_g^+$ state with triplet states ($^3\Pi_g$ and $^3\Sigma_g^-$). The relatively small anisotropy parameter values indicate that they are very likely formed via indirect predissociation process of CS$_2$. On the other hand, the observed differences in TKERs among three $J$ components may indicate that the nonadiabatic coupling very likely takes place via two different pathways. Future experimental studies as well as theoretical calculations are needed to precisely reveal the mechanism.

IV. CONCLUSION

In this work, the $S(^3P_{J=2,1,0})$ spin-orbit dissociation channels from CS$_2$ photodissociation near 204 nm have been investigated using the velocity ion imaging technique. Vibrational state resolved images were measured at four photolysis wavelengths from 201.36 nm to 206.61 nm. The total kinetic energy releases were obtained. In addition, the CS($X^1\Sigma^+$) co-product vi-
brational state distribution and product angular distributions were derived. The difference in TKERs observed in the $^3P_J=2,1,0$ channels suggests that there may be a relatively complex dissociation process. Nonadiabatic coupling plays an important role for the formation of $^3P_J=2,1,0$ + CS($^1\Sigma^+$) channels in UV region. By using the velocity map imaging technique combined with the VUV detection laser, here we reveal the UV photodissociation information about CS$_2$ molecules with higher resolution. The study of these channels can possibly be beneficial in the study of photodissociation dynamics.

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