Photodissociation Dynamics of OCS Near 128 nm: S(3P, J=2,1,0), S(1D2) and S(1S0) Channels

Si-wen Wang, Dao-fu Yuan, Wen-tao Chen, Ling Tang, Sheng-rui Yu, Xue-ming Yang, Xing-an Wang

a. Hefei National Laboratory for Materials Science at the Microscale and Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China
b. Hefei National Laboratory for Physical Science at Microstructure and Surface, University of Science and Technology of China, Hefei 230026, China
c. State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
d. School of Science, Southern University of Science and Technology, Shenzhen 518055, China

(Dated: Received on October 16, 2019; Accepted on November 29, 2019)

Here we report the study of the photodissociation dynamics of carbonyl sulfide in the vacuum ultraviolet region using the time-sliced velocity map ion imaging technique. Images of S(3P, J=2,1,0), S(1D2) and S(1S0) products were measured at four photolysis wavelengths of 129.32, 128.14, 126.99, and 126.08 nm, respectively. Four main dissociation channels: S(3P, J=2,1,0)+CO(X1Σ+), S(3P, J=2,1,0)+CO(A3Π), S(1D2)+CO(X1Σ+)+S(1S0)+CO(X1Σ+), and S(1S0)+CO(X1Σ+) channels, have been clearly observed and identified. Vibrational states of the CO co-products were partially resolved in the experimental images. From these images, the product total kinetic energy, the branching ratios and angular distributions of products have been derived. While the S(3P, J=2,1,0)+CO(A3Π) product channel is formed through the adiabatic dissociation process after the excitation to the (3Σ+) state, the results suggest that strong nonadiabatic coupling plays an important role in the formation of other three channels.

Key words: Vacuum ultraviolet photodissociation, Carbonyl sulfide, Velocity map ion imaging

I. INTRODUCTION

Carbonyl sulfide (OCS) plays an important role in atmospheric and planetary chemistry [1–3]. Both the natural and anthropogenic OCS molecules are the significant precursor in the sulfur cycle process [4–6]. Furthermore, investigations on photodissociation dynamics of OCS can be very helpful in understanding the ozone depletion process [7].

Over the past decades, much attention has been drawn in the study of OCS photodissociation, both in experiment and theory. In 1975, using an H2 lamp, Black et al. [8] measured the quantum yield of the S(1S) products from OCS at the photolysis wavelength between 110 nm and 170 nm by detecting the intensity of the radiative transition S(1S0→3P1). Later on, based on the results of laser induced fluorescence spectroscopy, Sivakumar et al. [9] found the photodissociation of OCS monomer mainly produces the S(3P) and S(1D) products, with the CO co-products rotationally excited and vibrationally cold at 222 nm. In 2011, Liptaic et al. [10] measured the S(1D2) polarization with high-resolution sliced imaging and observed individual rotational states of the CO(J) co-fragment at 235 nm.

Tremendous efforts have been made to study the dynamics of OCS photodissociation particularly in the UV region [11–13]. On the other hand, investigations on the photodissociation dynamics of OCS in the VUV region are relatively fewer. Using an excimer laser light, researchers can carry out experimental studies at specific fixed photolysis wavelengths. For instance, in 2006, Lee et al. studied the S(1D) products channel in the photodissociation of OCS at the photolysis wavelength of 193 nm using the dc slice imaging method [14]. In 2011, Wu et al. [7] studied the S(1S) product channel in the photodissociation of OCS using the velocity map imaging technique.

With the fast development of the modern laser techniques, tunable VUV laser light becomes possible. Recently, we have studied the carbon atom elimination channel in VUV photodissociation of OCS [15]. Both the conventional nonadiabatic pathways and roaming pathway are found to play a role in the dissociation process. Photolysis wavelength dependent behavior has
also been observed in the angular distribution. Here we report the study of sulfur atom products channels including S(^3P), S(^1D) and S(^1S) channels in the photodissociation of OCS at the photolysis wavelengths from 129.32 nm to 126.08 nm. Vibrational states of the CO co-products were partially resolved in the measured images. Four main dissociation channels, S(^3P_J=2,1,0)+CO(X^1 Σ^+), S(^3P_J=2,1,0)+CO(A^3Π), S(^1D_J)+CO(X^1 Σ^+) and S(^1S_J)+CO(X^1 Σ^+), have been clearly observed and identified. The product total kinetic energy releases, the branching ratios, and angular distributions of products have also been derived. This study will be helpful in understanding the nonadiabatic dynamics in the photodissociation process of small molecules.

II. EXPERIMENTS

The experimental setup has been described in detail previously [15–19]. In brief, OCS molecules (5% seeded in Ar) was supersonically expanded by a pulsed valve (Parker Series 9) with a 1 mm orifice. The repetition rate was 20 Hz and the stagnation pressure was 1 bar. Before entering the detection chamber (background pressure: 5×10^{-8} mbar), a skimmer with 1.5 mm diameter aperture was used to collimate the OCS molecular beam. The velocity of molecular beam was vertical to the circular electrodes.

A VUV and a UV laser light were employed as the photolysis and probe light in this study. Two Nd:YAG lasers were used to pump dye lasers. Two dye lasers, dye laser 1 and dye laser 2 were pumped by the first Nd:YAG laser (Continuum Powerlite 9020). The output of dye laser 1 (Corbra-Stretch, Sirah) was doubled to generate a 212.5 nm (ω_1) laser light (1.5 mL/pulse). A second visible laser light (ω_2) (5 mL/pulse) was generated by the dye laser 2 (Corbra-Stretch, Sirah). The two laser lights (ω_1 and ω_2) were spatially and temporally overlapped and focused into a stainless steel cell (filled with Kr gas). A VUV laser light (2ω_1−ω_2) was generated after a four wave mixing process. This VUV laser light was used to photolyze the OCS molecules. The polarization direction of the photolysis laser was parallel to the circular electrodes of the ion optics. Another UV laser light (ω_3) at 1 mL/pulse was generated by doubling the laser output of a third dye laser (dye Laser 3, Corbra-Stretch, Sirah) which was pumped by the second Nd:YAG laser (Continuum Powerlite 9020). This UV laser (ω_3) served as a detection laser and the resonance-enhanced multiphoton ionization (REMPI) scheme was used to detect the S atom products [20–22].

The counter propagated VUV and the UV laser overlapped in the center of the ion optics and crossed with the OCS molecular beam [23, 24]. After the VUV photodissociation of OCS, the S atom products were state-selected ionized by the detection laser light and then accelerated by the ion optics. The ions were detected by a position-sensitive, 70-mm diameter dual microchannel plate (MCP) coupled with a phosphor screen (P43). A 30 ns gate pulse was applied to the MCP to carry out the time slicing. A charge-coupled device (CCD) camera (Imager pro plus 2M, LaVision) was used to acquire images on the phosphor screen. Delay generators (DG 645 Stanford Research System) were used to control all the timings. Doppler scanning of ω_3 was performed to measure all the S atom products with different velocities.

III. RESULTS AND DISCUSSION

The images of S(^3P_2), S(^1D_2) and S(^1S_0) products were measured at four photolysis wavelengths, namely 129.32, 128.14, 126.99, and 126.08 nm, respectively. The results at the photolysis wavelength of 128.14 nm are shown in FIG 1. The red arrow in FIG 1 shows the polarization direction of the photolysis laser. A series of concentric rings in FIG 1 correspond to the different vibrational states of the CO co-products. For the S(^3P_J=2) products, two main features can be clearly identified: the inner rings with smaller velocities correspond to the S(^3P_J=2)+CO(A^3Π) product channel, and the outer rings with larger velocities correspond to the S(^3P_J=2)+CO(X^1 Σ^+) product channel. For the S(^1D_2) and S(^1S_0) channel, the CO co-products all populated in the electronic ground state X^1 Σ^+. Vibrational states can be partially resolved in the images.

A. Product total kinetic energy releases

The total kinetic energy release distributions (TKERs) were derived from the images by integrating signals over the full angular range. The following equation describes how a TKER of the dissociated products was acquired.

TKER = E_{hv} − D_0(OC−S) − E_{int}(CO) − E_{int}(S)

where E_{hv} represents the energy of the photolysis laser, D_0(OC−S) represents the bond energy of the C−S bond, E_{int}(CO) is the internal energy of CO products, and E_{int}(S) is the energy difference between the S atom products and the ground state S(^3P_2).

DOI:10.1063/1674-0068/cjcp1911179 ©2020 Chinese Physical Society
The total kinetic energy release distributions of $S(^3P_{J=2,1,0})$, $S(^1D_2)$ and $S(^3S_0)$, at the photolysis wavelength of 128.14 nm are shown in FIG. 2. Based on the energy conservation law, the total kinetic energy release was fitted by using a multi-peak fitting method. In general, the vibrational quantum states of the CO($X^1\Sigma^+$) products are highly excited. Since the internal energy of $S(^3P_{J=2,1,0})$ products is lower than the $S(^1S_0)$ and $S(^1D_2)$ products, there is more available energy for CO vibrational states in the $S(^3P_{J=2,1,0})$+CO channel. As a result, the vibrational excited CO states (CO($A^2\Pi$)) can also be populated and have been observed in $S(^3P_{J=2,1,0})$+CO channel. Because the $S(^3P_{J=2,1,0})$+CO($A^2\Pi$) channel is overlaid in the TKERs with a few high vibrationally excited states of the $S(^3P_{J=2,1,0})$+CO($X^1\Sigma^+$) channel, it is difficult to derive the intensity of the two channels accurately. So the uncertainty about intensity of the last few vibrational states of $S(^3P_{J=2,1,0})$+CO($X^1\Sigma^+$) channel may be larger.

As shown in FIG. 2, the intensities of $S(^3P_{J=2,1,0})$+CO($A^2\Pi$) channels are much higher and sharper than the $S(^3P_{J=2,1,0})$+CO($X^1\Sigma^+$) channels. For the $S(^3P_{J=2})$+CO($X^1\Sigma^+$) channel, with the increasing of the vibrational quantum number, the intensity varies very smoothly and reaches the first maximum at about $v=18$. After a small decrease, the intensities reach the second maximum at about $v=22$ which shows similar intensity to that of CO($X^1\Sigma^+$), $v=18$). For the $S(^3P_{J=1})$+CO($X^1\Sigma^+$) channel, the intensity increases even more slowly compared to the $S(^3P_{J=2})$+CO($X^1\Sigma^+$) channel. In contrast, the intensities of $S(^3P_{J=0})$+CO($X^1\Sigma^+$) show more oscillatory structures. In FIG. 2 (a-c), it is easy to identify different vibrational states in the CO($A^2\Pi$) channel. For the $S(^3P_{J=2})$+CO($A^2\Pi$) channel, the intensity of the $v=0$ state is similar to the $v=1$ state. For the $S(^3P_{J=1,0})$, the strongest state is CO($A^2\Pi$, $v=1$) which is slightly higher than the $v=0$ state. The intensity of CO($A^2\Pi$, $v=2$) is very small that it is hard to resolve. For the $S(^1D_2)$+CO($X^1\Sigma^+$) channel, CO ($X^1\Sigma^+$, $v=15$) is the most populated state, then the population decreases smoothly. The most populated vibrational state for $S(^3S_0)$ channel are $v=10$.

B. Product angular distribution

The angular distribution of the products has been derived and the anisotropy parameters are shown in FIG. 3. The following equation can be used to describe the product angular distribution in the photodissociation process.

$$I(\theta) = \frac{1}{4\pi} (1 + \beta P_2(\cos\theta))$$

(1)

In the above equation, $\theta$ represents the angle between the polarization direction of the photolysis laser and the velocity vector of the recoil product, $P_2(\cos\theta)$ is the second Legendre polynomial, and $\beta$ represents the anisotropy parameter. The $\beta$ values range from $-1$ to $2$.

For the $S(^3P_{J=2,1,0})$+CO($X^1\Sigma^+$) channel, as the structures of single vibrational state of CO product are not as distinct as other channels, it is not easy to accurately determine the $\beta$ values at specific vibrational states. Therefore, only the average anisotropy parameters of CO($X^1\Sigma^+$), $v=0-25$ were derived. The average anisotropy parameters of $S(^3P_{J=2,1,0})$+CO($X^1\Sigma^+$) channel ranges between $-0.8$ and $0$ at the four photolysis wavelengths. For the $S(^3P_{J=2,1,0})$+CO($A^2\Pi$) channel, as shown in FIG. 3, the state-specific $\beta$ values at the same wavelength are similar. They change between $-0.7$ and $0$. The distinction of anisotropy parameters between different vibrational states is not significant for the $S(^1S_0)$ and $S(^1D_2)$ channel.

C. Product branching ratios

By using the multi-peak fitting for the TKERs, the branching ratios of different vibrational states can be acquired. We estimate the error is about $\pm10\%$. For
The population of vibrational states CO($^3P$) in (a–c) S($^3P_{J=2,1,0}$)+CO($A^3\Pi$), (d) S($^1D_2$)+CO($X^1\Sigma^+$), and (e) S($^1S_0$)+CO($X^1\Sigma^+$) channels at all four photolysis wavelengths.

For the S($^1D_2$)+CO($X^1\Sigma^+$) channel (see FIG. 4(g)), the population increases smoothly at first, and stay for a moment, then decrease. At the wavelength of 126.08 nm, the branching ratio of $v=9$ and 10 are much higher than the other wavelengths. The population of $v=10$ is about 0.26 which is stronger than the population of the highest populated states at other wavelengths.

To obtain detailed information on the photodissociation dynamics, a deep understanding of potential energy surfaces is required. Over the past decades, both experimental and theoretical studies have been carried out on the photodissociation of OCS in UV region [25, 26]. There have been experimental and theoretical studies about potential energy surfaces [27], absorption spectrum [28], and isotope dependence [29]. In particular, for the higher energy region, a high resolution absorption spectrum and electron-impact spectroscopy [30] was performed at the energy from 4.0 eV to 10.8 eV. The ground OCS has a linear structure and belongs to the $C_{\infty v}$ point group [31]. The electronic configuration of OCS in the ground state is OCS ($X^3\Sigma^-$). While the bent structure of OCS belongs to the $C_2v$ symmetry and the ground state of that is $1^1\Delta'$ [32]. In a previous study [15], the potential energy curves has also been derived. It suggests that the photon excitation energies studied in this work correspond to the excitation to the $3^1\Sigma^+$ state which gives adiabatically the S($^3P_{J=2,1,0}$)+CO($A^3\Pi$) product. This channel shows very strong vibrational state resolved peak in the images. It is worth to mention that the $\beta$ values in this adiabatic channel are relatively small and are not significantly different from all other three channels indicating this dissociation process is not very fast. Meanwhile, the nonadiabatic channels: S($^3P_{J=2,1,0}$)+CO($X^3\Sigma^+$), S($^1S_0$)+CO($X^1\Sigma^+$), and S($^1D_2$)+CO($X^1\Sigma^+$) channels which are not adiabatically correlated to the initial excited state $3^1\Sigma^+$ also takes place in the dissociation process. The production of these three pathways has to undergo certain nonadiabatic pathways. The branching ratios of CO($A^3\Pi$) and CO($X^1\Sigma^+$) in the S($^3P_{J=2,1,0}$)+CO channel has shown the contribution of the nonadiabatic channel is significant when all vibrational states are considered. It is clear that for the S channels, as well as the previous studied C channel, due to the complexity of the potential energy surfaces, nonadiabatic dissociation channels are very important in the VUV photodissociation.

IV. CONCLUSION

We have studied the photodissociation dynamics of OCS by time-sliced velocity ion imaging technique in VUV region. Images of S($^3P_{J=2,1,0}$), S($^1D_2$) and S($^1S_0$) products were measured at four photolysis wavelengths, from 129.32 to 126.08 nm. Four channels are measured and identified in this work, S($^3P_{J=2,1,0}$)+CO($X^3\Sigma^+$), S($^3P_{J=2,1,0}$)+CO($A^3\Pi$), S($^1D_2$)+CO($X^1\Sigma^+$), and

Photodissociation Dynamics of OCS near 128 nm

FIG. 4 Product branching ratios of vibrational states in CO($X^1\Sigma^+$) for (a, c, e) S($3^3P_J=2; 1; 0$) + CO($X^1\Sigma^+$), (g) S($1^3D_2$) + CO($X^1\Sigma^+$), (h) S($1^3S_0$) + CO($X^1\Sigma^+$) channels and CO($A^3\Pi$) for (b, d, f) S($3^3P_J=2; 1; 0$) + CO($A^3\Pi$) channels at all photolysis wavelengths.

S($1^3S_0$) + CO($X^1\Sigma^+$). The total kinetic energy releases and the vibrational state specific anisotropy parameter $\beta$ values were measured at different photolysis wavelengths (from 129.32 nm to 126.08 nm). Besides that, the branching ratios of different vibrational states of CO were also derived. Strong nonadiabatic couplings are found to play an important role in the VUV photodissociation of OCS.

V. ACKNOWLEDGMENTS

This work was supported by the National Key R&D Program of China (No.2016YFF0200500), the National Natural Science Foundation of China (No.21473173, No.2150802, No.21327001 and No.21773213), the Strategic Priority Research Program of Chinese Academy of Sciences (No.XDB17000000), and the Fundamental Research Funds for the Central Universities.


DOI:10.1063/1674-0068/cjcp1911179 ©2020 Chinese Physical Society