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# Infrared laser kinetic spectroscopy of a photofragment CS generated by photodissociation of CS<sub>2</sub> at 193 nm: Nascent vibrational–rotational– translational distribution of CS

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Carbon monosulfide fragments generated by  $CS_2$  photodecomposition at 193 nm were examined by time-resolved observation of their vibration-rotation spectral lines with infrared diode laser kinetic spectroscopy. The CS molecules were found to be initially spread over a wide range of vibrational and rotational levels which were accessible with available energy, for both the triplet and singlet channels leading to sulfur atoms in the <sup>3</sup>P ground and <sup>1</sup>D excited states, respectively. The analysis of the observed line shape has allowed us to obtain information also on translational energy of CS fragments and to distinguish the contributions of the two channels. The branching ratio was thus estimated to be approximately one to one.

# INTRODUCTION

Photolysis of carbon disulfide has attracted much attention.<sup>1-7</sup> One of the themes of considerable interest is the branching ratio; when the photolysis is carried out at 193 nm or nearby wavelength, two channels are energetically possible:

$$CS_{2} + h\nu(193 \text{ nm}) \rightarrow CS(X^{1}\Sigma^{+}) + S(^{3}P)$$
  

$$\Delta H = -45.1 \text{ kcal/mol}, \qquad (1a)$$
  

$$\rightarrow CS(X^{1}\Sigma^{+}) + S(^{1}D)$$
(11)

 $\Delta H = -18.7 \text{ kcal/mol}. \quad (1b)$ 

Previous studies monitored either CS fragments by observing laser induced fluorescence,<sup>2,4,6</sup> absorption spectrum,<sup>1</sup> or chemiluminescence,<sup>2,5</sup> or S fragments through the observation of fluorescence  $({}^{1}D_{2})^{3}$  or resonance-enhanced photoionization  $({}^{3}P_{2})$ .<sup>7</sup> Time-of-flight (TOF) mass spectrometry was also employed to derive the nascent distribution of CS fragments.<sup>4,6</sup> The groups which monitored CS molecules favored the singlet channel, namely its contribution was estimated to be 0.80 and 0.60, as reported in Refs.4 and 6, respectively. On the other hand, two groups which focused attention to sulfur atoms arrived at reversed results: 0.15 with the upper limits of 0.30 and 0.26, as described in Refs. 3 and 7, respectively. Dornhöfer et al.<sup>5</sup> have pointed out that CS fragments prepared in vibrational states with v'' > 5 may be decomposed into  $C({}^{3}P)$  and  $S({}^{3}P)$  by second excimer laser photon, thereby favoring the singlet and triplet channels when CS and S were monitored, respectively.

Kanamori *et al.*<sup>8,9</sup> have recently developed infrared laser kinetic spectroscopy and have applied it to a number of photochemical processes.<sup>10</sup> This method consists of infrared diode laser spectroscopy combined with excimer laser photolysis and allows us to observe vibration–rotation transitions of photofragments with the time resolution of about 0.5  $\mu$ s. In view of the discrepancies among the previous studies on the branching ratio of the CS<sub>2</sub> photodecomposition channels, we have applied infrared kinetic spectroscopy to CS photofragments. Because infrared diode laser spectroscopy provides us with much more detailed information on vibra-

tion-rotation levels of CS than LIF employed in the previous studies, it was expected to shed light on the photodecomposition process of  $CS_2$  at 193 nm.

#### EXPERIMENTAL

The infrared (IR) diode laser kinetic spectroscopy system employed in the present study has been described in detail elsewhere.<sup>8,9</sup> The diode laser beam passed 12 times through a 2 m long White-type multiple-reflection cell. The excimer laser beam (hereafter referred to as the UV beam) which was unfocused was introduced in the cell nearly coaxially with the IR beam through a fused silica window placed on the front frange of the cell and crossed the IR beam at a very small angle (1°-2°) around the central part of the cell. Because of this finite crossing angle, the effective path length of the IR beam was about 12 m.

The IR signal, after detected, was fed into a transient digitizer consisting of  $1024 \times 8$ -bit memory channels with the minimum sampling time of 50 ns/channel and was then transferred to a 16-bit desk-top computer, which acted as either a 1024-channel signal averager or three sets of dual gated integrators. Subroutines were written in ASSEMBLER language and were linked with a FORTRAN system to control the direct memory access (DMA) and signal accumulation processes; the repetition rate of sampling signals could be increased up to 50 Hz without introducing any special devices.

In order to record the line shape, the diode laser frequency was locked to a fringe of a free-spaced Fabry–Perot étalon and was scanned slowly by introducing air gradually in (or pumping air out from) the étalon; when the pressure was changed from 0 to 760 Torr, as monitored by an MKS Baratron, the wave number was decreased by about 0.3  $cm^{-1}$ , which was large enough to record a line. Conversion from pressure to wave number and correction for any nonlinear scanning were carried out by the computer.

A sample of  $CS_2$  with the stated purity of 99.6% was used without any further purification. Carbon disulfide was introduced in the cell through a port located around the central part of the cell and was pumped out from another port near the rear end of the cell, while Ar was flowed into the cell through the third port attached to the front frange in order to keep the window for the UV beam clean. It was found that the position where the UV beam was most strongly absorbed could be displaced throughout the cell by adjusting the amount of Ar flow. The CS signals were strongest when  $CS_2$ and Ar pressures were adjusted so as to observe strong blue emission from most central part of the cell. The nascent distribution of CS was, however, determined by keeping the sample pressures as low as possible at the expense of intensity, in order to avoid the effect of rotational relaxation.

#### RESULTS

Because CS fragments could be distributed over a wide range of vibrational and rotational levels, the transition frequencies were calculated using the data obtained by microwave<sup>11</sup> and infrared diode laser<sup>12,13</sup> spectroscopy. Figure 1 shows an example of the observed spectrum recorded using the dual gated integrator mode: the sample employed was 6 mTorr of CS<sub>2</sub> diluted with Ar of 1 Torr and the gate width was 2  $\mu$ s. About 200 lines were observed; the vibrational quantum number involved ranged from v = 0 to v = 11 and the rotational quantum number from J = 3 to J = 123.

Then, the time profile of each line was examined in order to determine the nascent distribution. It was found that, for many lines, the time profile was quite different for different parts of the absorption line. The top trace of Fig. 2 shows an example of the v = 4-3, J = 99-98 transition; the spectrum was recorded with the CS<sub>2</sub> and Ar pressures of 2 and 100 mTorr, respectively. It clearly shows that the signal at the line center starts as an emission for about 1  $\mu$ s, then changes to an absorption reaching a maximum at around 4  $\mu$ s, and decays within 20  $\mu$ s. This behavior may be contrasted with that of the signals obtained at  $\pm$  100 MHz off from the center. They show sharp rise in absorption and decay somewhat faster than the center signal.



FIG. 1. The bottom trace shows a part of the observed spectrum of CS generated by photodecomposition of CS<sub>2</sub> at 193 nm. The partial pressure was 6 mTorr and 1 Torr for CS<sub>2</sub> and Ar, respectively, and the gate width was  $2\mu$ s. The middle trace represents a spectrum of N<sub>2</sub>O used as a wave number standard and the top trace shows fringes from an étalon with a free spectral range of about 0.01 cm<sup>-1</sup>.

A time-resolved spectrum was then recorded by using three sets of dual gates, as depicted in the middle part (b) of Fig. 2. The first set A consists of two gates, one starting at t = 0, i.e., the time when the excimer laser is switched on and lasting for 1  $\mu$ s and the other being also of 1  $\mu$ s width, but preceding the first one by  $2 \mu s$ . The set B is also made of a pair of 1  $\mu$ s gates, one being delayed 1  $\mu$ s from and the other being initiated 3  $\mu$ s earlier than the laser shot. In the last set C the gates are 10  $\mu$ s, one being started 2  $\mu$ s after and the other being ended  $3 \mu s$  before the laser pulse. In each set the difference between the two signals obtained from a pair of gates was recorded, in order to eliminate any slow fluctations of the base line. An example of the spectrum thus obtained is reproduced in the bottom trace (c) of Fig. 2. As expected from the top trace (a) of Fig. 2, gate A gives a shallow emission at the center accompanied by strong absorptions in both sides (A of the bottom traces). This line shape is still preserved in the gate B stage, but the center is



FIG. 2. (a) Time profiles of the v = 4-3, J = 99-98 transition of CS, one (1) at the center frequency and the other two (2,3) at frequencies about  $\pm 100$  MHz off the center. It is to be noted that trace (1) starts as an emission for about 1  $\mu$ s after the photolysis, whereas traces (2) and (3) show sharp rises of absorption. The traces were obtained by integrating signals for 1000 laser shots. The partial pressure was 2 and 100 mTorr for CS<sub>2</sub> and Ar, respectively. (b) Three pairs of gates for the observation of time-resolved spectra. The time scale is the same as that of Fig. 2(a): gate A is 1 $\mu$ s width with no delay, gate B 1 $\mu$ s width with 1 $\mu$ s delay, and gate C 10 $\mu$ s width with 2 $\mu$ s delay. (c) Time-resolved spectra of the v = 4-3, J = 99-98 transition of CS recorded using three sets of dual gates shown in Fig. 2(b). The spectra were obtained by subtracting the signal of the preceding gate from the signal of the following gate.

already changed to absorption. Gate C gives an ordinary Doppler-broadened Gaussian line shape. These observations are explained in the next section in terms of Doppler effect.

# ANALYSIS

The available energy, which is defined to be the energy of the excimer laser photon  $E_{h\nu}$  minus the dissociation energy of a C-S bond of  $CS_2D_0$  estimated by Okabe<sup>14</sup> to be  $102.9 \pm 0.32$  kcal/mol, may be allocated to the vibrational and rotational energies of CS, the translational energy of CS and S, and the excitation energy  $E_{elec} = E({}^{1}D) - E({}^{3}P)$ when the sulfur atom is prepared in the  $^{1}D$  state. (As mentioned in the Discussion, the thermal energy of the precursor  $CS_2$  was taken into account in analyzing the observed spectrum.) Because we are observing a particular vibration-rotation transition of CS and we are focusing attention to either the singlet or the triplet channel, the translational energy must take a definite value for both the upper and lower states of the transition because of conservation of energy, except for uncertainties due to the thermal (mainly rotational and translational) energy the  $CS_2$  molecule would have before the photolysis and to the spread in energy of the excimer laser photon.

The previous TOF experiments<sup>4,6</sup> have shown that the photofragments CS and S are ejected isotropically in space. A CS molecule formed in a particular vibrational-rotational level specified by the quantum numbers v and J will have a velocity vector which is distributed over the surface of a sphere, as shown in Fig. 3(a). This distribution is converted to Doppler shifts when observed using an IR laser beam as a probe, namely to a square-shaped population distribution for both the upper and lower states, as illustrated in Fig. 3(b). The width of the square distribution corresponds to the Doppler shift compatible with the available energy and the area of the square to the population in a vibrationalrotational level. Because the upper state of a transition has less translational energy than the lower state, the spectrum which is proportional to the difference in the populations of the two states will take a form shown at the bottom of Fig. 3(c), i.e., the central part may become negative, as observed for the v = 4-3, J = 99-98 transition [see Fig. 2(c)]. The square distribution will be modified by the spreads in both CS<sub>2</sub> thermal energy and excimer-laser photon energy. These effects were found to be well taken into account by convoluting the distribution with a Gaussian function.

Figure 4 shows a plot of the vibrational and rotational energies of CS in two dimensions and indicates the regions which are allowed for CS fragments to occupy when generated by the two channels, singlet and triplet. Four transitions are represented by arrows for which the observed Doppler profiles are reproduced in Figs. 5(A)-5(D). The first example is the v = 10-9, J = 74-73 transition, for which only the lower state can be reached by CS molecules prepared by the triplet channel. In fact, as shown in Fig. 5(A), the observed line shape is of simple Gaussian type. The width of the square shown in the figure represents the total Doppler width for the lower state, the v = 9, J = 73 level. The observed line shape was analyzed by the least-squares method,



FIG. 3. (a) Velocity distribution of CS fragments in the center-of-mass coordinate system; a CS molecule in the lower state of a transition specified by the vibrational and rotational quantum numbers v and J has a larger velocity, as indicated by a larger circle, than a CS molecule in the upper state with v + 1 and  $J \pm 1$ . (b) Population distributions of the upper and lower states as functions of Doppler shifts expressed in a frequency scale. (c) The Doppler-broadened line shape of a vibration-rotation transition.

by fixing the width of the square to a theoretical value estimated from energy conservation and by convoluting the square distribution with a Gaussian function. The simulated curve thus obtained is drawn in the figure by a solid line.

The second example, the v = 9-8, J = 66-65 transition



FIG. 4. Vibrational and rotational levels of CS fragments plotted in a twodimensional plane; both the vibrational and rotational axes are linear in energy. CS fragments generated by the  $CS_2$  photolysis at 193 nm may be distributed in the lower left regions of the respective broken lines when they are generated together with singlet (<sup>1</sup>D) and triplet (<sup>3</sup>P) sulfur atoms. Four arrows marked by A, B, C, and D represent the transitions of which the time-resolved spectra are given in Fig. 5.

ABSORPTION



FIG. 5. (A) v = 10-9, J = 74-73; (B) v = 9-8, J = 66-65, (C) v = 5-4, J = 42-41 and (D) v = 4-3, J = 31-30 transitions of CS. The dotted curves represent the spectra observed with gate A of Fig. 2(b), i.e., no delay and 1  $\mu$ s width. The square "line shapes," the widths of which correspond to the Doppler effects of CS, are convoluted with a Gaussian function to take into account the spreads in thermal energy of the precursor CS<sub>2</sub> and in excimer-laser photon energy, and the simulated line shapes thus obtained are drawn by solid curves.

still lies in the region where only the triplet channel is opened, but, in this case, both the upper and lower states can be populated. The observed line shape confirms this expectation, as shown in Fig. 5(B); it has two absorption peaks separated by a small valley of emission, as in the case of v = 4-3, J = 99-98 shown in Fig. 2. The third example, the v = 5-4, J = 42-41 transition, represents a more complicated situation; here not only the triplet, but also the singlet channel are allowed, but the upper state is accessible merely with CS molecules generated by the triplet channel. The widely spread part of the signal is primarily due to the triplet channel, whereas the strong central peak is mainly ascribed to the singlet channel. This example clearly shows that we may distinguish contributions of the two channels.

The last example, the v = 4-3, J = 31-30 transition, affords a most complicated case; both the upper and lower states are populated by CS molecules of both the singlet and triplet channels. Because the transition is located far away



FIG. 6. Nascent distribution of CS fragments over vibrational and rotational levels. The abundance of molecules generated by the triplet channel is designated by a stick and that of molecules through the singlet channel by a stick with an open circle at the top.

from the triplet limit, the Doppler effect becomes nearly equal for the upper and lower states in the case of the triplet channel. Therefore, the triplet signal becomes weak, making it somewhat difficult to assess the contribution of the triplet channel.

We have analyzed the time profiles of 100 transitions and have derived the nascent population of CS molecules in each vibration-rotation level. The result is illustrated in Fig. 6, where the population in each level is designated by a stick.

#### DISCUSSION

One of the most important results obtained by the present study is that a detailed analysis of the Doppler profile allows us to determine the upper-state and lower-state populations separately. This may be contrasted with the results obtained by an ordinary technique of spectroscopy, which provides only the difference between the populations of the two states involved in the transition observed. The present case is complicated by the presence of two reaction channels, but the method developed in this study made it possible to discriminate CS fragments generated by the two processes. It should also be pointed out that the analysis of the observed spectra could have been performed by assuming CS fragments to be distributed nearly isotropically in space, as supported by the previous TOF results<sup>4,6</sup> that the CS<sub>2</sub> molecule is predissociated by 193 nm excitation.

The available energy  $E_{h\nu} - D_0$  is calculated to be 15 740 cm<sup>-1</sup> for the triplet channel (all sulfur atoms of the triplet channel were assumed in the present study to be prepared in the <sup>3</sup>P<sub>2</sub> ground state), and it is smaller for the singlet channel by  $E_{elec} = 9240 \text{ cm}^{-1}$ , i.e., it is equal to 6500 cm<sup>-1</sup>. The observed data indicate that CS fragments reached vibrational and rotational levels higher in energy than these limits by up to 650 cm<sup>-1</sup>. For example, the v = 5-4, J = 42-41 transition was really observed for the singlet channel also. This excess energy is probably ascribed to the rotational and translational energies of the precursor CS<sub>2</sub>; two rotational and three translational degrees of freedom of CS<sub>2</sub> would accommodate energy of about 500 cm<sup>-1</sup> at room temperature. The analysis was carried out by increasing the available energy by  $650 \text{ cm}^{-1}$ .

As described in detail in Refs.8 and 9, the present detection system has the response time of about 0.5  $\mu$ s. If the sample pressure is too high, the initial processes would be difficult to observe. So the pressure was reduced as low as possible, paying special attention to any changes of the signal with pressure. As a close examination of Figs.5 might indicate, the observed data points reveal slight tendency of being closer to the line center than the simulated curves. These observations may be caused by translational relaxation, but its effect, if any, is too small to affect the present results.

It has been found that the fundamental band was very difficult to observe, because the lifetime of CS in v = 0 was too long to apply the present time-resolved observation method; an extremely low repetition rate would be necessary for observing this band.

The previous studies<sup>2,4</sup> using LIF or TOF to monitor CS fragments have concluded that the vibrational population of CS peaks at v = 3. If this is correct, we should observe most lines of the v = 3-2 and 2–1 bands as emissions, as in the case of SO produced from SO<sub>2</sub>.<sup>8</sup> However, this was not the case at all; all the observed lines appeared as absorptions. Small emission signals observed at the central part of some lines are always overtaken by absorptions in the wings.

The present results summarized in Fig. 6 show that the singlet and triplet channels are nearly equally important. Although the number of quantum states 680 available for CS molecules generated by the triplet channel exceeds 225 by the singlet channel, the population in each state is clearly larger for the singlet channel. It is thus concluded that the branching ratio of the two channels is approximately one to one. As mentioned in the Introduction, Dornhöfer *et al.*<sup>5</sup> proposed that the CS molecules in the  $X^{1}\Sigma^{+}v'' > 5$  states were photodecomposed by a second photon of the excimer laser, in order to remove the discrepancies among the previous studies of the CS<sub>2</sub> ArF laser photolysis. However, no abrupt changes were observed in the present study between the nascent populations of CS in v = 5 and v = 6. Furthermore, no CS molecules could be detected beyond the triplet

channel limit. The Doppler profiles of CS molecules in each vibrational state were found to be very close to those which were just expected from one photon dissociation of  $CS_2$ . The present observation thus indicates that the CS photodecomposition and excitation processes discussed in Ref.5, if any, do not play important roles under the conditions of the present study. The present conclusion is supported by a recent result obtained by Endo *et al.*<sup>15</sup> using millimeter- and sub-millimeter-wave kinetic spectroscopy.

It is a little surprising that the spin-forbidden triplet channel makes so much contribution to photodissociation of  $CS_2$  at 193 nm. This is probably due to the fact that electronic states to which  $CS_2$  is initially excited by 193 nm radiation acquire triplet character to a considerable extent, favoring the triplet channel of dissociation.

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