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Ultraviolet photodissociation study of CH₃SCH₃ and CH₃SSCH₃

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The photodissociation processes of CH_3SSCH_3 at 248 and 193 nm and CH_3SCH_3 at 193 nm have been studied by translational spectroscopy. When excited at 248 nm, CH_3SSCH_3 undergoes a simple S–S bond scission to produce two CH_3S fragments with an average translational energy of 33 kcal/mol. The angular distribution of the product with respect to the polarized laser is measured and fitted with an anisotropy parameter $\beta=1.2$. It indicates that the dissociation is a fast, direct process. At 193 nm, there is only a simple dissociation channel for CH_3SCH_3 , while CH_3SSCH_3 undergoes a predominant C–S bond scission with the S–S bond scission as a minor channel. No angular dependence for the primary products from both CH_3SCH_3 and CH_3SSCH_3 has been observed. The observation of S_2^+ time-of-flight spectra shows that a major fraction of CH_3S_2 , which is internally excited when produced, undergoes spontaneous dissociation to form slow S_2 and CH_3 radicals. Results obtained for the dissociation processes of both molecules at 193 nm are rationalized and comparisons with previous investigations [J. Chem. Phys. **92**, 6587 (1990); **95**, 5014 (1991)] are also included.

I. INTRODUCTION

Both CH₃SCH₃ and CH₃SSCH₃ molecules have received considerable interest during the past decades in connection with the role in the atmospheric sulfur cycle and the acid precipitation problem. Because of the need to assess details of the acid formation, increasing efforts have been made in the areas of spectroscopic studies¹⁻³ and kinetic measurements^{4,5} of the active intermediates as well as the mechanism of atmospheric oxidation^{6,7} of these species.

The UV absorption spectra⁸⁻¹³ of CH₃SCH₃ and of CH₃SSCH₃ consist of progressions of vibronic bands and broad continuous bands, respectively, and many active intermediates can be produced when the parent molecules are photolyzed. Callear and Dickson¹⁴ reported from their early measurements by UV flash photolysis centered at ~195 nm that a simple rupture of the C–S bond was the only important process for CH₃SCH₃ through reaction (1)

$$CH_3SCH_3 \rightarrow CH_3S + CH_3.$$
 (1)

As for CH_3SSCH_3 , there were two competing dissociation channels

$$CH_3SSCH_3 \rightarrow CH_3S + CH_3S \tag{2}$$

and

$$CH_3SSCH_3 \rightarrow CH_3S_2 + CH_3. \tag{3}$$

The dissociation product CH_3S_2 was not directly observed, but inferred from the observation of the transient species S_2 , which exhibited a similar time dependence as the major species CH_3S and CH_3 . The existence of S_2 was rationalized in that it was formed by a unimolecular decomposition of vibrationally excited CH_3S_2 via

$$CH_3S_2 \rightarrow S_2 + CH_3. \tag{4}$$

The relative degree of S–S to C–S scission was determined to be about 1.35. At about the same time, Rao *et al.*^{15,16} performed a similar experiment in the wavelength region of 200–300 nm, but observed only the processes of Eqs. (1) and (2).

Direct detection of the CH_3S_2 radical from CH_3SSCH_3 was not made until most recently by Nourbakhsh *et al.*¹⁷ using translational spectroscopy. At 193 nm, they detected not only the primary dissociation processes (2) and (3), but also the secondary dissociation channel (4) by assuming that the additional photon was absorbed on the basis of the experimental fact that the threshold of flight time for S_2^+ in the time-of-flight (TOF) spectrum was substantially lower than that for $CH_3S_2^+$. Thus, the formation of S_2 from CH_3S_2 in the latter study was attributed to a mechanism which was different from the previous interpretation.¹⁴ They also observed^{17,18} this type of secondary dissociation for the primary CH_3S fragment produced from pulsed reactant beams of CH_3SCH_3 and CH_3SSCH_3 at 193 nm.

In our present study, we also employ translational spectroscopy to investigate the photodissociation processes of CH₃SCH₃ excited at 193 nm and that of CH₃SSCH₃ at 248 and 193 nm. The product TOF spectra at several beam angles are taken with a cw beam system whose nozzle is at an elevated temperature. The possible interference of clusters is then eliminated in this study. It is then possible to extract a full product translational energy distribution P(E) for the dissociation processes given in Eqs. (1)-(4). Apart from this improvement, additional information is also obtained by measuring the product angular dependence with respect to the polarization of laser light. The results show that CH₃SSCH₃ undergoes a simple dissociation to produce fast CH_3S radicals anisotropically for Eq. (2) when it is excited at 248 nm. For both molecules excited at 193 nm, products formed in accord with Eqs. (1)-(3) show no angular dependence, indicating that the dissociation is more complicated at this higher photon energy. The power dependence of the S_2^+ TOF spectrum indicates that a large amount of slow S_2 product is produced by a unimolecular decomposition of internally excited CH₃S₂. Thus, our direct detection of CH₃S₂, S₂, and CH₃ fragments confirms the mechanism proposed in Eq. (4) by Callear and Dickson.¹⁴

II. EXPERIMENT

The rotatable beam apparatus and the experimental procedure employed in the present study have been described in detail elsewhere.¹⁹ Briefly, the reactant beam was produced by bubbling the helium carrier gas through a liquid sample in a thermostat to have a mixture of either $\sim 10\%$ CH₃SCH₃ or $\sim 5\%$ CH₃SSCH₃ for a total pressure of 350 Torr. It was expanded through a nozzle oven at a temperature of about 150 °C with an opening slit of 0.013 cm in diameter. No further purification except freeze–pump–thaw degasing was made for both chemicals whose stated purities were 99% (Merck).

The velocity distribution of the cw reactant beam was always measured before and after the photoexperiments with a spinning disk housed in front of the detector entrance slits. The measured speed profile of reactant species was then fitted to an assumed functional form^{20,21} $f(v) \sim v^2 \exp[-(v-v_0)^2/\alpha^2]$, where v_0 is the most probable speed and α is a measure of the width of speed profile. These constants were determined to be $v_0=1.32\times10^5$ cm/s and $\alpha=1.55\times10^4$ cm/s for CH₃SCH₃, and $v_0=1.35\times10^5$ cm/s and $\alpha=1.35\times10^4$ for CH₃SSCH₃, respectively.

The particle detector consisted of an electron impact ionizer, a quadrupole mass filter, and a Daly ion counter. The ionizer, normally operated at 120 eV, was located 36.6 cm away from the photon-molecule crossing region. A multichannel scaler of 1024 channels, interfaced with a PC, recorded the arrival time of the ion signal relative to the photolysis laser pulse to obtain a TOF spectrum. A dwell time of 2 or 1 μ s per channel was typical. For the product TOF measurements, an ion intrinsic time inside the detector t_r had to be subtracted to get a real time for the actual flight of the photofragments. The ion flight time in this study was determined to be $4.0m^{1/2}$ in units of microseconds, with *m* being the detected ion mass in amu.

The light source was an excimer laser (Lambda-Physik LPX 100), which had an average output of 100 mJ/pulse for KrF running at 100 Hz and 75 mJ/pulse for ArF at 55 Hz, respectively. The laser beam was focused with a fused silica lens to a size of $\sim 0.1 \times 0.3$ cm² at the center of the photon-molecule crossing area. For the measurements of product angular distribution, the size of the laser beam was first reduced by an iris diaphragm and then polarized by a stack of eight quartz plates set at the Brewster angle. At 248 nm, this linearly polarized light was then rotated in 20° increments by a half-wave retarder. At 193 nm, the product angular dependence was measured with the electric vector ϵ of the linearly polarized light either parallel or perpendicular to the detection axis. The average power in angular dependence measurements was adjusted until no saturation effect was ob-



FIG. 1. TOF spectra (O) of CH_3^+ and CH_3S^+ when CH_3SCH_3 is photodissociated at 193 nm. The solid lines were obtained from the P(E) curve shown in Fig. 2.

served for each ion fragment. The degree of polarization for the present setup was determined experimentally to be 85%.

III. RESULTS AND DISCUSSION

A. CH₃SCH₃ at 193 nm

0.5

RELATIVE INTENSITY

1. TOF spectra of CH₃S and CH₃

From the TOF measurements, the relative kinetic energy of the fragments in the center-of-mass (c.m.) coordinate system E_t can be deduced. By the law of the conservation of energy

$$E_{avl} = h \nu + W_{int} - D_0 = E_t + E_{int}, \qquad (5)$$

where $h\nu$ is the photon energy, W_{int} is the internal energy of the reactant, and D_0 is the dissociation energy for the ground state reactant, we can determine the partitioning of the available energy E_{av} into product translational energy E_t and internal excitation energy E_{int} .

For CH₃SCH₃ photodissociated at 193 nm, TOF spectra were collected for CH₃⁺ ions at 10° and for CH₃S⁺ ions at beam angles ranging from 10° to 30°. Figure 1 depicts the typical spectra of CH₃⁺ and CH₃S⁺ at 10° and 20°, respectively. The measured values are given in open circles, while the solid curves were derived from a P(E) distribution for Eq. (1). A forward simulation method²¹⁻²⁴ was used for the curve fitting procedure. This was done first by transforming an assumed P(E) function to the laboratory coordinate and followed by convoluting with the experimental functions, such as beam velocity, beam angular divergence, viewing angle for the detector, and effective length of the ionizer. The simulation procedure was iterated until a best fit to the mea-

a) CH₃+/10°



FIG. 2. Deduced P(E) distribution for the photodissociation of CH₃SCH₃ at 193 nm.

sured data was obtained. Figure 2 shows the resultant P(E) distribution with an average energy of 43 kcal/mol and a full width at half-maximum of 27 kcal/mol.

As can be seen clearly from Fig. 2, our results produce a P(E) distribution to give a full account of the slow (or internally excited) fragments, which were missing in the results of Ng and his colleagues.¹⁸ This difference stems from the fact that they used a high concentration of reactant flux via a pulsed valve, whereas we applied a continuous beam with a nozzle at an elevated temperature. Thus, the cluster interference is absent in the present work and we are able to measure the product TOF spectra at smaller beam angles so no slow moving fragments could escape detection. On the other hand, Ng and his co-workers had better signal-noise ratio in TOF spectra for the determination of the maximum kinetic energy. Apart from these differences, the major features of both P(E) curves are essentially identical to each other.

Having had a complete description of the P(E) distribution, further insight into the partitioning of the excess energy for the reaction can be readily exploited. Using the C–S bond energy of 75 kcal/mol,^{18,25} the fraction of the translational partition of the total available energy f_t is calculated to be 59% if the internal energy W_{int} of the parent molecule is neglected in Eq. (5). Thus, the dissociation products may be excited internally as much as 30 kcal/mol. Furthermore, this amount of energy has to be widely distributed among the various internal modes of the products as expected from the broad P(E) distribution. Although the geometry of CH₃S does not change appreciably from the molecule to the free radical, one expects that CH₃S should be excited vibrationally as the C-S bond length is first lengthened by about 0.04 Å at the excited states^{9,10} and followed by a decrease of about 0.04 Å when the radical is produced.¹ Similarly, vibrational excitation is also expected for the formation of a planar CH₃ radical. In addition, since the C_{2v} symmetry is pre-served during the transition,^{9,10} the products should also be rotationally excited by a torque exerted onto the fragments as they move apart. Consequently, there must exist a strong coupling between the translational and internal modes on the exit channel for the product fragments in Eq. (1).

Besides the major dissociation process [Eq. (1)], we

have found no evidence of other photofragments for CH₃SCH₃ excited at 193 nm. On the contrary, Ng and his co-workers¹⁸ observed not only the dissociation channel of $CH_3SCH_3 \rightarrow CH_3SCH_2 + H$, but also a secondary process of $CH_3S + h\nu$ (193 nm) $\rightarrow CH_3 + S(^3P, ^1D)$ at the laser energies of 90-120 mJ/pulse. With a large ambient background of $m^+/e=1$ in the detection chamber, we have decided to measure $CH_3SCH_2^+$ at a 10° beam angle. At this beam angle, we should be able to observe this ion species on the basis of the translational energy derived for this dissociation channel (Fig. 7 of Ref. 18). Despite a careful search, however, we have failed to collect the CH₃SCH₂⁺ signal. Neither have we observed the evidence of sequential two-step dissociation process from the CH_3^+ or S^+ TOF spectrum. The absence of these minor dissociation processes, whose quantum yields were estimated to be less than 10%, is attributed to the consequence of low laser energy of 75 mJ/pulse employed in the present study.

2. Polarization effect on the formation of CH₃S

The angular distribution of the dissociating products in the c.m. coordinate has the functional form²⁶

$$I(\theta) \sim 1 + \beta P_2[\cos(\theta - \theta_0)], \tag{6}$$

where θ is the angle between the electric vector ϵ of the laser light and the product c.m. recoil direction, and $P_2(\cos \theta)$ is the second degree Legendre polynomial. The anisotropy parameter β contains all dynamical information about the dissociation process; it equals 2 for a pure parallel transition and -1 for a pure perpendicular transition. The constant θ_0 is defined as an angular shift for each beam angle selected in a rotatable beam apparatus.^{21,24} Its magnitude depends on the reactant speed v_0 and the speed of recoiling fragment in the c.m. coordinates. With $v_0 = 1.32 \times 10^5$ cm/s measured for CH_3SCH_3 and 1.36×10^5 cm/s for the CH_3S fragment, which is equivalent to the average energy of 43 kcal/mol obtained in the P(E) determination, θ_0 is estimated to be about 20° if the CH₃S⁺ TOF spectrum is taken at a 20° beam angle. Since this value is far from the magic angle (54.7°) of the $P_2(\cos \theta)$ function, by simply varying the electric vector $\boldsymbol{\epsilon}$ of the laser beam either parallel or perpendicular to the detection axis, we should be able to observe the polarization effect if the dissociation proceeds rapidly. Accordingly, the polarization measurements for CH_3S^+ were performed at a 20° beam angle with a laser energy of 25 mJ/pulse. At this energy, the total integrated counts of TOF spectra was linearly proportional to the laser energy.

Within the limits of our experimental accuracy, results for these measurements produced no variation in the total integrated counts of the TOF spectrum. It indicates that for CH₃SCH₃ excited at 193 nm, the dissociation products recoil without preferential direction. The present observation is not totally unexpected as there are so many excited states involved in the transition. The absorption spectrum for the CH₃SCH₃ at 193 nm is rather congested, consisting of Rydberg transitions with extensive vibrational progressions resting upon a broad underlying continuum.⁸⁻¹² The transition in this region has been assigned^{10,11} as the promotion of an electron from an n_s (3 b_1) orbital to either a $4pb_1({}^1A_1)$



FIG. 3. TOF spectra (O) of CH_3S^+ ion at three beam angles when CH_3SSCH_3 is photodissociated at 248 nm. The solid curves were derived from the P(E) distribution given in Fig. 4.

Rydberg orbital or a $4sa_1/9a_1^*({}^1B_1)$ orbital. In other words, these excited states are of the mixed Rydberg-valence configurations. In view of the excited states involved in the energy of interest, we suggest that the present results of insensitivity to the polarization of the laser light could have arisen either from an excitation to a long-lived Rydberg state or from a mixture of parallel and perpendicular transitions, followed by the crossing to the nearby unknown predissociating state.

B. Ch₃SSCH₃ at 248 nm

1. TOF spectra of CH₃S

Figure 3 depicts the typical CH_3S^+ TOF spectra collected at 10°-30° beam angles for CH_3SSCH_3 photodissociated at 248 nm; the open circles are the measured values, while the solid curves are derived from the P(E) distribution for Eq. (2) shown in Fig. 4 by the same forward convolution method.^{22,23} The resultant P(E) distribution led to an average kinetic energy of ~33 kcal/mol with a maximum threshold energy at 47±2 kcal/mol. The uncertainty was calculated from the averaged value of four separated runs for the beam angles from 10° to 50°. With this improved accuracy, the S-S bond strength for CH₃SSCH₃ can be evaluated from the threshold energy of the P(E) distribution and the internal energy W_{int} in Eq. (5).

Following the usual treatment used for a supersonic beam, we only consider the vibrational contribution to W_{int} and ignore the rotational effect. For a nozzle temperature kept at 150 °C, W_{int} was calculated to be 2.7 kcal/mol with vibrational frequencies taken from Ref. 27. Accordingly, a maximum energy of 70±2 kcal/mol for the S-S bond in the

CH₃SSCH₃ molecule was obtained. This value is in good agreement with the published data of 67.8 \pm 2 (Ref. 25) and 72.4 \pm 1.5 kcal/mol.¹⁷

Besides the CH_3S^+ ion signal, we have also detected CH_2S^+ , S^+ , and CH_3^+ TOF spectra at a 10° beam angle. These ion signals were treated as the daughter fragments from the CH₃S radical in the ionization chamber since they all appeared about the same time as the CH₃S⁺ signal. However, neither a $CH_3S_2^+$ nor a S_2^+ ion was detected. Since the S-S bond is stronger than the C-S bond in CH₃SSCH₃ by an amount of about 15 kcal/mol,¹⁷ the absence of these two ion species implied that the dissociation occurred via a bondselective process. These results are markedly different from the conclusion of Kumar et al.,²⁸ who probed the timeresolved absorption spectra of the transient species produced in a static cell. They claimed that two major dissociation channels CH_3S+CH_3S and $S_2+C_2H_6$ had taken place when CH₃SSCH₃ was photolyzed at 248 nm or by a CO₂ laser with \sim 40% of the total yield attributed to the second process. Our direct detection of the dissociation product, however, gave no evidence for this dissociation channel.

2. Anisotropy of CH₃S

A whole angular distribution was measured for a CH_3S^+ ion at a 10° beam angle and with a laser energy of 15 mJ/ pulse by varying the angle of the polarization of the laser light at a 20° increment. Figure 5 shows the measured results; it is plotted as the normalized total integrated counts for each TOF spectrum vs the polarization angle with respect to the detection axis, where 0° is defined as the polarization of the laser light parallel to the detection axis.

A forward simulation^{21,24} was employed to determine the anisotropy parameter β in Eq. (6). The simulation procedure was carried out with the known P(E) distribution in Fig. 4 to reproduce the TOF spectrum taken at each polarization angle by an assumed β value. The computation was iterated until the best fits to all TOF spectra with a common β value were found. The fitted curves shown in Fig. 5 were obtained with β =1.2±0.2 and with angular shift θ_0 adjusted to 10°. It clearly indicates that CH₃SSCH₃ undergoes a fast S–S bond rupture after the excitation via a parallel transition. Further-



FIG. 4. Deduced P(E) distribution for the photodissociation of CH₃SSCH₃ at 248 nm.



FIG. 5. Angular distribution of CH_3S^+ when CH_3SSCH_3 is photodissociated at 248 nm measured with 15 mJ/pulse laser power and at a 10° beam angle. The solid curve was derived with anisotropy parameter β =1.2; the dashed and the dash-dot curves were given for comparison with β =1.0 and 1.4, respectively.

more, based on our calculated bond strength, f_t is found to be 70%, which is about the same order of magnitude (68%) predicted by a simple impulsive mechanism.^{29,30} The positive β value combined with a large f_t value strongly support that the dissociation for CH₃SSCH₃ at 248 nm [Eq. (2)] is a rapid, bond-selective process.

The CH₃SSCH₃ molecule has a C_2 symmetry^{31,32} and its absorption band^{12,31} shows a maximum at 250 nm, a shoulder ~220–230 nm, and a comparatively sharp band at about

195 nm. The first band has been attributed to the promotion of a nonbonding electron on the sulfur atom to an antibonding orbital localized on the S-S bond $\sigma_{ss}^* \leftarrow n_s$ with a partial $4s \leftarrow n_s$ Rydberg transition. Thus, the observation of the anisotropy parameter $\beta=1.2$ is consistent with these assignments and the dissociation could have arisen directly from the excited ¹B state. The present results obtained for CH₃SSCH₃ excited at 248 nm are quite similar to those found for H₂O₂ photodissociated at 266, 248, and 193 nm.^{33,34} Both molecules are observed to undergo a direct dissociation process with a large fraction of the total available energy released as product translation. While the parallel transition for CH₃SSCH₃ is observed in this study, vibrationally unexcited OH radicals are produced from H₂O₂ with a transition moment perpendicular to the O-O bond.

C. CH₃SSCH₃ at 193 nm

1. TOF spectra of primary products

We measured the TOF spectra for $CH_3S_2^+$, S_2^+ , CH_3S^+ , S^+ , and CH_3^+ ions when CH_3SSCH_3 was excited at 193 nm. Figure 6 depicts the typical spectra collected for $CH_3S_2^+$, S_2^+ , CH_3S^+ , and CH_3^+ at a 20° beam angle; the open circles are the normalized experimental data. These TOF spectra show clearly that there exist a single ion peak for $CH_3S_2^+$ and S_2^+ , two for CH_3S^+ , and three for CH_3^+ with the appearing time properly matched to one another. Thus, the dissociation processes of Eqs. (2) and (3) can be uniquely identified; for instance, the three major peaks of the CH_3^+ ions in Fig. 6(d)



FIG. 6. Product TOF spectra collected for CH₃SSCH₃ photodissociation at 193 nm and a 20° beam angle. Two competing dissociation channels [Eqs. (2) and (3)] were clearly identified: (a) TOF spectrum of CH₃S₂, a product of Eq. (3), (b) the major signal of S_2^+ produced from CH₃S₂, (c) the first peak produced from CH₃S of Eq. (2) and the second peak from CH₃S₂; and (d) the second major peak from Eq. (2), while the other two peaks produced from the coproducts of CH₃ and CH₃S₂ of Eq. (3). Each individual line was derived from the *P*(*E*) distributions presented as solid curves in Figs. 7(a) and 7(b) (see the text for discussion).



FIG. 7. The P(E) distributions for CH₃SSCH₃ dissociation processes at 193 nm. (a) The solid curve for CH₃S production of Eq. (2). (b) The solid curve obtained from the simulation of the CH₃S₂⁺ spectrum of Fig. 6(a) for Eq. (3), while the dashed line obtained from the best fits of the first peak of CH₃⁺ spectrum of Fig. 6(d); the hatched area indicates the uncertainty. (c) The P(E) curve for the formation of S₂ and CH₃ from CH₃S₂; the hatched area was shown with the stated uncertainty in (b) as well as those introduced in the secondary process.

are produced by the electrons of 120 eV in the ionizer, and they can be associated with the photoproducts of CH₃, CH₃S, and CH₃S₂ in the order of appearance. To ensure that these ion signals were free from the cluster interference, experiments were repeated with the nozzle temperature lowered from 150 to 66 °C. At the latter temperature, additional ion signals showed up at ~360 μ s for CH₃S⁺ TOF spectra collected at the beam angles of 10° and 20°. We also observed similar signals at about the same time for other ion masses at a 10° beam angle, indicating that there was the interference of the clusters at this low temperature. We therefore conclude that the TOF spectra collected at a temperature of 150 °C in Fig. 6 are real.

To find out the P(E) distributions for the dissociation processes of Eqs. (2) and (3), a similar forward convolution procedure, as described in Sec. III A, was employed. The P(E) distribution for Eq. (2) was first found from the best fits to the first peak of CH_3S^+ in Fig. 6(c) and the second ion signal of CH_3^+ in Fig. 6(d). Figure 7(a) depicts the P(E)curve with an average kinetic energy of 33 kcal/mol, which is equivalent to $f_t=41\%$ by using the S-S bond energy derived earlier in this work. It is noted that the average kinetic energy is the same as that found at 248 nm, hence a large amount of CH_3S must be internally excited at this high photon energy, as shown in Figs. 4 and 7(a).

Next we discuss the more complicated problem of the

search for a P(E) distribution for the dissociation process given in Eq. (3). The simulation was done initially by fitting the $CH_3S_2^+$ spectrum shown in Fig. 6(a) with a P(E) distribution displayed as the solid curve in Fig. 7(b). However, this P(E) distribution produced a poor fit to the first ion peak of Fig. 6(d), which was attributed to the coproduct CH₃ in Eq. (3); the calculated values were appreciably smaller than the measured data at the late times $\sim 100 \ \mu s$. Thus, the failure of finding a single P(E) distribution for the dissociation process of Eq. (3) has to be checked if a fraction of nascent CH₃S₂ fragments undergoes a secondary dissociation in accord with Eq. (4). More S_2^+ TOF spectra were measured at various laser powers to confirm the existence of Eq. (4). In these measurements, the dependence of the integrated S_2^+ ion signal with respect to the laser energy was observed to be linear at 20 mJ/pulse. Figure 8 depicts the typical spectra with laser energy at 75 and 10 mJ/pulse shown as solid and open circles, respectively. It clearly indicates that almost 85% of the slow S_2 ion signal at high laser power originated from the same mechanism as that at low laser power, or the major source of the slow S_2^+ ions was the spontaneous decomposition¹⁴ of CH₃S₂. We shall return to this subject in the following section.

Consequently, the P(E) distribution for Eq. (3), obtained by using the $CH_3S_2^+$ TOF spectrum of Fig. 6(a) has to be corrected. The simulation was then repeated by assuming that the first peak of the CH_3^+ spectrum in Fig. 6(d) was produced entirely from the coproduct CH_3 in Eq. (3). The P(E) distribution resulted from this simulation is displayed as the dotted curves in Fig. 7(b); the hatched area represents the range of uncertainty due to the incompleteness in resolving the first ion peak from the second in the CH_3^+ spectrum. The corresponding fit to the measured data is given as the dash-dot curve in Fig. 9(a), where the measured data were reproduced from Fig. 6(d). The simulation process for Eq. (3) was arrested at this point and the final P(E) curve produced an average kinetic energy of 30±3 kcal/mol. Taking 55 kcal/mol for the C-S bond strength in CH₃SSCH₃,¹⁷ we obtained $f_t = 32\%$ and an average amount of 63 kcal/mol was partitioned into internal excitation.



FIG. 8. Power dependence of S_2^+ TOF spectra produced from photodissociation of CH₃SSCH₃ at 193 nm (the solid circles are for 75 mJ/pulse and the open ones are for 10 mJ/pulse).



FIG. 9. The overall best fits of product TOF spectra collected for CH_3SSCH_3 photodissociated at 193 nm and 20° beam angle. The measured spectra (O) were the same as for Figs. 6(a)-6(d): (a) CH_3^+ ; (b) S_2^+ ; and (c) CH_3S^+ . The symbols for the calculated curves:—generated from the solid P(E) curve in Fig. 7(a) for Eq. (2);---from the solid P(E) curve in Fig. 7(b);------from the dot curve in Fig. 7(b);-------from the solid curve in Fig. 7(c); and------obtained from Eq. (7) of producing an electronic excited CH_3S radical.

2. Secondary dissociation of CH₃S₂

As discussed above, the product internal excitation of 63 kcal/mol in Eq. (3) was calculated directly from the dotted curves of P(E) distribution shown in Fig. 7(b). This value should be corrected, when applied to the secondary dissociation process in Eq. (4), by the difference between the solid and the dotted curves that represents the fragments actually participating in the secondary dissociation. This gave an average internal excitation of about 80 kcal/mol rather than 63 kcal/mol for the CH₃S₂ reacted in the secondary dissociation. Taking 47.5 kcal/mol as the C-S bond energy recommended for the CH₃S₂ radical,³⁵ it is more than sufficient to undergo a spontaneous dissociation if most of the available energy is deposited into this radical. On the other hand, the S-S bond scission in CH₃S₂ is not expected since it has a bond energy of 83 kcal/mol.³⁵ Thus, the conclusion in the last section that CH₃S₂ undergoes a spontaneous decomposition is justified.

A similar forward simulation method^{22,23} was also employed for this secondary process. However, the computation becomes more complicated and less accurate than the primary process because now the velocity distribution of the parent beam has to be replaced by a distribution function obtained from the difference between the solid and the dotted curves in Fig. 7(b). Besides, since the uncertainty associated with the hatched area in Fig. 7(b) is rather high, the combined effect of these two factors would introduce, at least, an equivalent amount of uncertainty in analyzing the secondary dissociation of CH_3S_2 fragments. The P(E) distribution derived from the fits to the S_2^+ spectrum is shown in Fig. 7(c), where a similar uncertainty is shown by the hatched area. The corresponding fits are given by the dash-dot-dot curve in Figs. 9(a) and 9(b). As was shown in Fig. 7(c), a unimolecular decomposition of CH₃S₂ is correctly reflected by the P(E) distribution with high probability density function at low energy. It must be noted, however, that the simulation was carried out on the basis of experimental data without considering the differentiation of the unimolecular decomposition and the possibility of a minor two-photon process. From the difference between the calculated fits of the dotted curve and the dash-dot-dot curve in the spectrum in Fig. 9(b), we estimated that approximately three quarters of the CH₃S₂ radicals would react in the secondary dissociation process.

As far as the curve fitting is concerned, the P(E) distributions obtained from the dissociation processes of Eqs. (2)–(4) are not sufficient for the slow ion signals to be observed ~260 μ s in the CH₃S⁺ spectrum shown in Fig. 9(c). There must exist another dissociation channel which is responsible for such additional signal. Since the S–S bond scission of CH₃S₂ is already regarded as an unlikely process, the following process which yields one of the CH₃S radicals in its first electronic state from the parent molecule in reaction (7)

$$CH_3SSCH_3 \rightarrow CH_3S(^2E) + CH_3S^*(^2A_1)$$
(7)

becomes the only choice. For the S–S bond energy of 70 kcal/mol derived in the present work and the first excited state energy of 76 kcal/mol (Ref. 1) for CH₃S^{*}, the one-photon dissociation process of Eq. (7) at 193 nm is still possible. Assuming that Eq. (7) indeed takes place, we have obtained a satisfactory fit to these slow ion signals which appeared mainly in the CH₃S⁺ TOF spectra shown as the long dashed curves in Fig. 9(c) with a P(E) distribution corresponding to an average kinetic energy of ~3.3 kcal/mol. Figure 10 depicts those ion signals S⁺₂, S⁺, CH₃S⁺, and CH⁺₃, taken at a 10° beam angle, to show the equally good fits produced from all dissociation processes discussed above.

The present results that CH₃S₂ undergoes predominantly a unimolecular reaction to produce CH₃+S₂ do not contradict the previous findings of the two-photon, two-step dissociation process by Nourbakhsh et al., ¹⁷ who carried out their experiments at high laser energies of 100-130 mJ/pulse. As discussed in the last section, the secondary dissociation process of CH₃S₂ by absorbing additional photon was also evident in the S_2^+ TOF spectra of Fig. 8 as we increased the laser energies from 10 to 75 mJ/pulse. Thus, there is no doubt about the presence of the second photon effect at high laser power, while our present results uniquely explain the fact that the CH₃S₂ fragments produced at 193 nm are very active and can be decomposed spontaneously to produce CH_3+S_2 . On the other hand, we have observed no clear evidence of the secondary process of $CH_3S + h\nu$ (193 nm) $\rightarrow CH_3 + S$ from both CH_3^+ and S^+ TOF spectra shown in Figs. 9 and 10. As they were taken at low laser power, it is not surprising that there is no second photon effect.



FIG. 10. TOF spectra for CH₃SSCH₃ photodissociated at 193 nm and at a 10° beam angle. Similar to Fig. 9, satisfactorily good fits to the measured spectra were obtained by the P(E) curves shown in Fig. 7 and Eq. (7) (see the figure captions in Fig. 9 for the symbol used in each individual curve).

3. Branching ratio between C–S and S–S bond scissions

Our discussion over experimental results has confirmed the dissociation processes of Eqs. (2)–(4) for CH₃SSCH₃ at 193 nm. In addition, a minor process of Eq. (7) in producing CH₃S* in its first electronic excited state is also included. It will be of interest to determine the branching ratio for the C–S and S–S bond scissions. The procedure involves the deduction of the ion signals in the laboratory coordinate by transforming to the c.m. coordinate to obtain the true signals. The TOF spectra of CH₃S₂⁺, S₂⁺, CH₃S⁺, S⁺, and CH₃⁺ ions taken at the same experimental conditions 16–20 mJ/pulse and a 10° beam angle are used with a computation scheme given by Lee and his colleagues.^{36,37} The atomic polarizability data necessary for the calculation were taken from Ref. 38.

The branching ratio for the fission of the C-S bond over the S-S bond was first calculated to be about 1.04 by ignoring the secondary dissociation of CH₃S₂. This ratio was based on the CH₃S⁺ TOF spectrum of Fig. 10(c) with the fast component attributed to CH₃S produced from Eq. (2), while the second component was attributed to CH₃S₂ from Eq. (3). An identical result was also obtained based on the S^+ spectrum of Fig. 10(b). When the fraction of CH_3S_2 that undergoes secondary dissociation was included, this ratio increased to 4.0. On the other hand, a direct computation based on the first two ion peaks in the CH_3^+ spectrum to reduce the uncertainty introduced by the secondary dissociation yields a value of 1.6. Thus, we obtain a range of 1.6-4.0 for the branching ratio evaluated from two different approaches. The variation arises mainly from the uncertainty introduced in the calculation for the P(E) distribution in Fig. 7(b) and the

deconvolution procedures of several composite TOF spectra. Although the uncertainty is large, we recommend the relative degree of C–S to S–S bond scission to be 2.8 ± 1.2 and conclude that the formation of CH₃S₂ and CH₃ is a predominant process when CH₃SSCH₃ is excited at 193 nm. This is in sharp disagreement with the results of Callear and Dickson¹⁴ who carried out the flash photolysis experiments with a broad bandwidth of 185–205 nm. The result of this early measurement yielded a different conclusion that the dissociation was dominated by the formation of CH₃S radicals.

Finally, as in the discussion for CH_3SCH_3 at 193 nm, our results of the P(E) distributions [Figs. 7(a) and 7(b)] give a complete description of the slow products, which were missing in the results of Ng and his co-workers.¹⁷ The observation of these slow particles provides not only the necessary information for the estimation of the relative degree of C–S and S–S bond scissions of CH_3SSCH_3 , but also the conclusion of spontaneous dissociation of the primary product CH_3S_2 .

4. Polarization effect

The product angular dependence for CH₃SSCH₃ excited at 193 nm was measured for CH₃S₂⁺, S₂⁺, and CH₃S⁺ ions at 10° beam angle. At this beam angle, the constant θ_0 in Eq. (6) was estimated from the P(E) distributions in Figs. 7(a) and 7(b) to be 10° and 18°, respectively, for CH₃S and CH₃S₂. Thus, it is worthwhile to run the polarization effect experiments. In these experiments, the laser energy was maintained at about 16–20 mJ/pulse. The results show that the TOF spectra of both CH₃S⁺ and CH₃S₂⁺ produce no

J. Chem. Phys., Vol. 100, No. 10, 15 May 1994 142.104.240.194 On: Tue, 16 Dec 2014 15:30:49 change in the total integrated counts, within our experimental limit of accuracy, for both parallel and perpendicular polarization directions.

The absorption spectrum^{12,31} of CH₃SSCH₃ has a strong broad band peaking at 196 nm. This band has been assigned to $\sigma_{ss}^* \leftarrow n_s$ and $\sigma_{cs}^* \leftarrow n_s$ transitions,³¹ suggesting that the excited states at the wavelengths of interest are in fact the repulsive states. The observation of no polarization effect for the major ion signals arising from the primary dissociation processes suggests that mixed parallel and perpendicular transitions could likely be involved. On the other hand, since we observed a large branching ratio in favor of the bond fission of the weaker bond C-S bond against the stronger S-S bond, the dissociation process could have lasted a prolonged period of time to allow the energy randomization. In other words, a coupling between the translation and the internal modes of the dissociating molecule could take place such that the P(E) distributions for the two major primary processes have a substantial fraction in the low energy range, as shown in Figs. 7(a) and 7(b). These P(E) distributions are significantly different from the one derived for a direct dissociation process of CH₃SSCH₃ excited at 248 nm, as shown in Fig. 4.

It would be of interest to make a remark here on the observation of the polarization dependence of the S_2^+ spectrum. There appeared a slight decrease in slow S_2^+ signals when the laser light was polarized parallel as compared with those taken unpolarized or polarized perpendicular. This observation is indirect evidence of a minor dissociation process for CH₃SSCH₃ by breaking up the two C–S bonds simultaneously when the available energy for the reaction is in excess of about 40 kcal/mol.¹⁷ However, since the difference in the total integrated counts of the polarization dependence is small and since more assumptions must be involved for analyzing the triple products, no further effort is attempted on this additional primary process.

IV. CONCLUSION

The major concern of this work is to elucidate the dissociation dynamics of CH_3SCH_3 and CH_3SSCH_3 from the observation of product TOF spectra and the angular dependence with respect to the polarization of the laser light. For CH_3SCH_3 photodissociated at 193 nm, only a single dissociation channel is detected with CH_3S and CH_3 as the products, which carry away an average translational energy of 43 kcal/mol. The polarization measurements for the CH_3S^+ spectra show that the products recoil isotropically. These results are discussed by a predissociation process from mixed Rydberg-valence states.

For CH₃SSCH₃ excited at 248 nm, we have observed a simple bond rupture of the S–S bond to produce two CH₃S radicals. The anisotropy parameter β =1.2±0.2 is determined with a product translational energy of 33 kcal/mol. This amount of energy is equivalent to f_t =70%, which is in good agreement with the prediction by classical impulsive mechanism and, therefore, it is treated as a direct dissociation process. At 193 nm, the dissociation processes for CH₃SSCH₃ become complicated; two primary dissociation channels re-

sulting from either the C–S or the S–S bond scission are observed with a branching ratio of about 2.8 in favor of the former case. About 80% of the CH_3S_2 fragments produced from the primary process contains sufficient internal energy to undergo a spontaneous dissociation into S_2 and CH_3 radicals. No polarization dependence has been observed for these major primary products and the dissociation processes are rationalized by mixed parallel and perpendicular transitions or an energy randomization prior to the dissociation.

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