

Multiphoton dissociation/ionisation of dimethyl sulphide (CH₃SCH₃) at 355 and 532 nm

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Abstract. Multiphoton dissociation/ionization has been studied for CH₃SCH₃ at 355 and 532 nm using a time-of-flight mass spectrometer. The major ion signals observed at 355 nm are C⁺, CH₃⁺, HCS⁺, CH₂S⁺, CH₃S⁺ and CH₃SCH₃⁺. Power dependence studies at 355 nm show a (2 + 1) REMPI process for the formation of parent ion. Peaks at *m/e* = 46, 47 and 61 show two-photon laser power dependence whereas *m/e* = 15 and 45 peaks show four-photon dependence. However, in 532 nm photoionisation, no parent ion signal is observed. A peak at *m/e* = 35 corresponding to SH₃⁺ has been observed. SH₃⁺ has been suggested to originate from CH₃SCH₂⁺ via a cyclic transition state. Photoionisation results of CH₃SCH₃ have been compared with those of CH₃SSCH₃ at these two wavelengths.

Keywords. Dimethyl sulphide, multiphoton ionization; time-of-flight mass spectroscopy.

1. Introduction

Dimethyl sulphide (CH₃SCH₃, DMS) is both a natural and industrial pollutant and accounts for approximately 25% of the total sulphur released into the atmosphere¹⁻⁵. It is also known to play a major role in the atmospheric sulphur cycle⁶. Due to these reasons a large number of studies have been carried out to understand the photodissociation of CH₃SCH₃⁷⁻¹². DMS could undergo dissociation via C–S and C–H bond cleavage as shown below.



Flash photolysis at 195 nm⁷ and photofragment translational spectroscopy studies⁸ at 193 nm on CH₃SCH₃ showed that primary process is the cleavage of C–S bond to give CH₃S and CH₃ radicals. However, Nourbakhsh *et al*⁹ detected C–S as well as C–H bond breaking in the photodissociation of DMS at 193 nm. Quantum yield of CH₃S formation

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in the photodissociation of CH_3SCH_3 at 193 nm was found to be $(0.78 \pm 0.10)^{10}$ which also indicated that C–S bond breaking is not the sole fragmentation channel. Tokue *et al*¹³ measured the dispersed fluorescence from DMS on 153 nm excitation and assigned the fluorescence to CH_3S ($A \rightarrow X$) transition. They concluded that for excitation in the 200–140 nm region, formation of electronically excited fragments from DMS is the predominant process.

A number of photoionisation studies have been performed for DMS using visible and ultraviolet laser radiations^{9,14–16}. Resonance-enhanced multiphoton ionisation experiments¹⁵ determined the ionisation potential for DMS to be (8.71 ± 0.005) eV whereas recent non-resonant two photon pulsed field ionisation studies¹⁷ reported a value of $70097.3 \pm 2 \text{ cm}^{-1}$ (8.69096 ± 0.00016 eV). Norbakhsh *et al*⁹ recorded the breakdown diagram for the formation of ions like $\text{CH}_3\text{SCH}_2^+$, CH_3S^+ and CH_2S^+ in the photoionisation of CH_3SCH_3 over the wavelength region of 90 to 147.5 nm. Syage *et al*¹⁴ reported that DMS when excited up to 10.8 eV using (1 + 1) REMPI at 227.9 nm (5.4 eV), showed mainly parent ion signal. However, for (2 + 1) REMPI at 407.4 nm (3.04 eV), in addition to the parent ion signal, extensive fragmentation was observed. According to these authors since the three-photon ionisation at 407.4 nm can produce low energy parent ions, the ion fragmentation must be due to ion absorption and dissociation from a fourth photon. However, from the photoelectron spectrum of DMS¹⁸, it is apparent that there is no energy state of the molecular ion around 3.04 eV which can be accessed by the molecular ion at this wavelength.

Although a number of studies have been carried out for DMS, the mechanism of formation of other ions like HCS^+ and SH_3^+ , reported in earlier studies^{11,14–16}, had not been discussed. In a related study of an analogous compound, dimethyl disulfide (CH_3SSCH_3 , DMDS)¹⁹ we have observed that DMDS when excited with 355 or 532 nm produced a large number of photofragment ions. However, no molecular ion signal was observed for DMDS. The most intense peak, observed at $m/e = 45$, was assigned to the formation of HCS^+ originating due to H_2 elimination from H_3CS^+ . In view of this, the objective of this study is to investigate the difference in the photo-processes of DMS and DMDS when both are excited at 355 and 532 nm under similar conditions and to explain the origin of different photofragment ions. Further, to establish that HCS^+ is indeed originated from H_3CS^+ , we have tried CH_3SCH_3 as another source of H_3CS^+ . Therefore, in the present work, we have investigated the multiphoton excitation of CH_3SCH_3 at 355 and 532 nm and the results are compared with those of DMDS.

2. Experimental

Experimental set up used for these studies has been described in detail in our previous publication²⁰. Briefly, the set-up consists of three chambers which are pumped by liquid nitrogen cooled diffusion pumps. The base pressure of the instrument is 1×10^{-6} Torr. In the first chamber, helium bubbled through dimethyl sulphide sample passes through a stainless steel tube and effuses out of a 0.5 mm nozzle. After collimating through 2 mm skimmer, which is placed at 1.5 cm distance from the nozzle, the sample enters the second chamber where it is subsequently ionised. The third chamber is perpendicular to the ionization chamber and is used as a flight tube for the ions. The flow rate of helium as carrier gas and the vapour pressure of dimethyl sulphide were controlled suitably to ensure that dimer and higher oligomers of dimethyl sulphide are not formed in the molecular beam. The dimethyl sulphide beam is ionised at the centre of the repeller and

extraction grids. The laser is aligned in such a way so that the molecular beam, the accelerating field and laser beams are orthogonal to each other and intersect at the centre. The excitation and ionization of the sample is carried out using third harmonic of a Nd:YAG laser (Quantel 980E, 355 nm, pulse duration = 6–8 ns). The laser radiation was focussed using a 35 cm focal length lens. Pulse energy was measured using an energy meter (Molelectron model PM 10V1). In this study the laser intensity in the ionisation region was in the range of 10^8 – 10^9 W/cm².

The time-of-flight (TOF) mass spectrometer is based on double-focused electric field ion source principle²¹ and was designed and built indigenously. The ions were accelerated into a 170 cm field free region and detected using a Chevron microchannel plate detector (Galileo Inc., Model 3025). The signal from the detector was amplified using a fast preamplifier and sent to a digital storage oscilloscope (LeCroy 9350A, 500 MHz) where it was averaged for typically 1000 shots and further processed on a computer. The oscilloscope is triggered by a photodiode placed near the ionisation zone to get correct flight time of different ions. The mass resolution ($M/\Delta M$) of this spectrometer is ~ 300 .

Dimethyl sulphide was purchased from BDH, with a stated purity of > 97% and was used as such without further purification except for few freeze-pump-thaw cycles. DMDS with a stated purity of > 99% was obtained from Fluka Chemie.

In our experiments, the same laser pulse is used for dissociation and ionization of the molecule (one colour experiments). Power dependence is estimated from the slope of a log–log plot of integrated ion signal vs laser energy which is indicative of number of photons required to excite/dissociate and ionise the molecule/fragments.

3. Results and discussion

3.1 Photoionisation at 355 nm

3.1a *Fragment ions*: Figure 1a shows time-of-flight mass spectrum of CH₃SCH₃ in 355 nm ionisation at a laser intensity of $\approx 10^9$ W/cm². The ion signals are found at $m/e = 12, 13, 14, 15, 32, 35, 45, 46, 47, 61$ and 62 which have been assigned to C⁺, CH⁺, CH₂⁺, CH₃⁺, S⁺, SH₃⁺, HCS⁺, CH₂S⁺, CH₃S⁺, CH₃SCH₂⁺ and CH₃SCH₃⁺. Peaks in the C₂H_{*n*} region are indicative of the existence of C–C bond for some of the ionised species.

An important difference in the results of DMS and DMDS has been the observation of the parent ion signal. DMS on 355 nm excitation produces a parent ion signal, whereas DMDS under identical conditions does not. It is to be noted that the most intense ion signal is for HCS⁺ ($m/e = 45$) and not for CH₃SCH₃⁺ or CH₃⁺ or CH₃S⁺ which are the dissociation/primary products. HCS⁺ is the main fragment ion at all the laser intensities employed. The relative abundance of $m/e = 47/45$ increases with decrease in laser intensity. Under similar experimental conditions, the TOFMS of CH₃SSCH₃ is shown in figure 1b. It can be seen that the parent ion signal is missing in this case, however, the peak at $m/e = 45$ (HCS⁺) is most intense in the $m/e = 44$ – 47 region and the pattern in this region is similar to that of DMS.

The ion signals in the region of $m/e = 12$ to 15 arise due to the dissociation of CH₃⁺ ions. Another important observation of the present study is the appearance of ion signals in the region of $m/e = 24$ to 29 due to the formation of C₂H_{*n*}⁺ species. Belbruno *et al*²² have also reported the formation of these ions during photoionisation of CH₃SeCH₃.

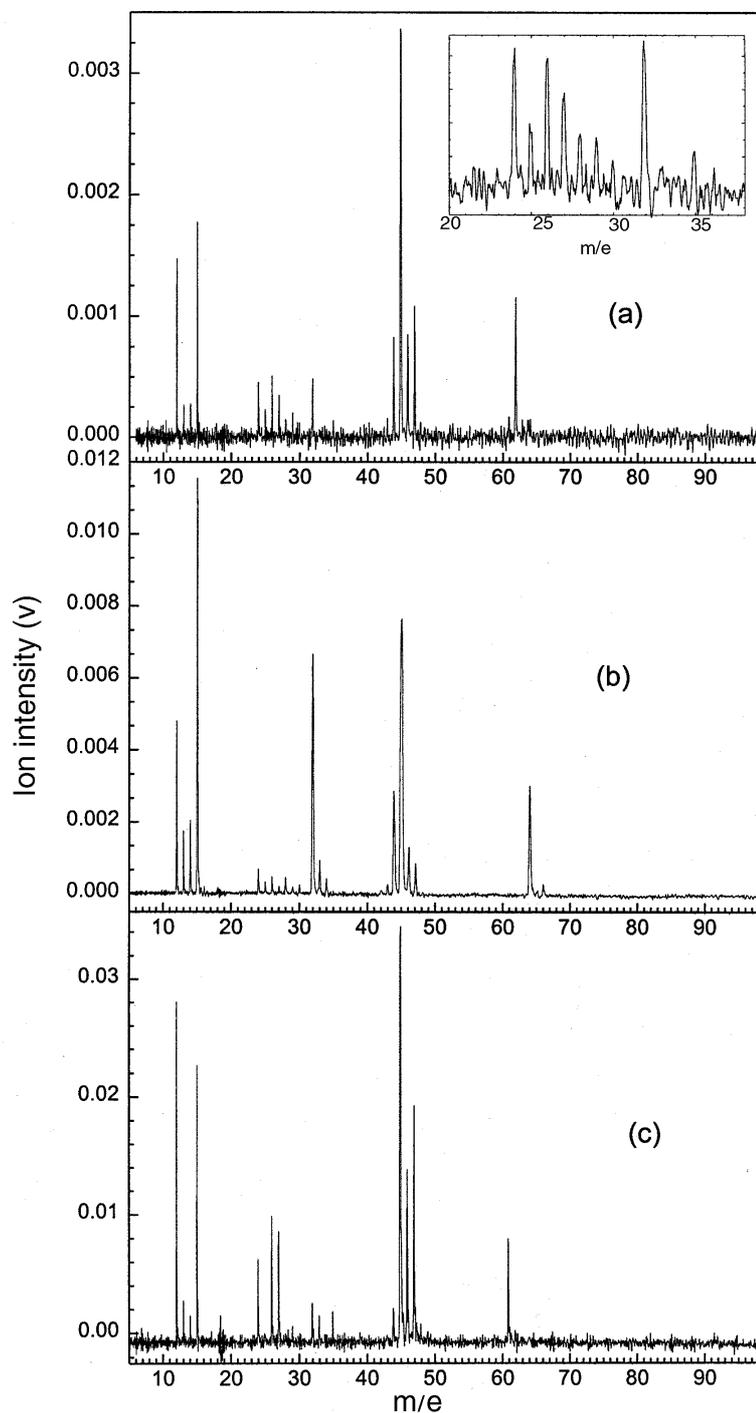
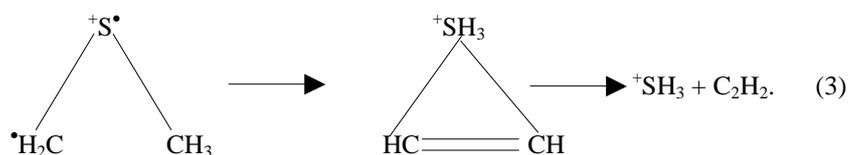


Figure 1. Time-of-flight mass spectrum at a laser intensity $\sim 10^9$ W/cm², (a) dimethyl sulphide (CH₃SCH₃) at 355 nm, (b) dimethyl disulphide (CH₃SSCH₃) at 355 nm, (c) dimethyl sulphide (CH₃SCH₃) at 532 nm.

These ions are produced by molecular ion isomerisation to form $\text{CH}_3\text{CH}_2\text{SH}^+$ and its subsequent fragmentation. The S^+ originates from the fragmentation of CH_3S^+ ions.

3.1b *Origin of SH_3^+* : The formation of SH_3^+ ($m/e = 35$) is clearly seen for CH_3SCH_3 (figure 1a inset and 1c) and not for CH_3SSCH_3 (viz. figure 1b) at either of the two wavelengths. There is no direct way of forming the SH_3 radical from CH_3SCH_3 which on subsequent ionisation gives SH_3^+ . This implies that SH_3^+ is a secondary product from some other ion. CH_3S^+ being common for both CH_3SCH_3 and CH_3SSCH_3 cannot be the source of SH_3^+ . Thus SH_3^+ can only originate from $\text{CH}_3\text{SCH}_2^+$ or $\text{CH}_3\text{SCH}_3^+$. Further, if $\text{CH}_3\text{SCH}_3^+$ was responsible for SH_3^+ then it should not be detected in case of 532 nm photoionisation (see §3.2) experiments as $\text{CH}_3\text{SCH}_3^+$ itself could not be detected at this wavelength. The results thus indicate that SH_3^+ is generated from $\text{CH}_3\text{SCH}_2^+$. This argument is further supported by the results of Chiang *et al.*²³ on CH_3SSCH_3 and Syage *et al.*¹⁴ on CH_3SCH_3 where they observed a signal at $m/e = 35$ along with that of $\text{CH}_3\text{SCH}_2^+$ at $m/e = 61$. To generate the SH_3^+ fragment, $\text{CH}_3\text{SCH}_2^+$ must go via a cyclic transition state as shown below.



Transition states of this type have been postulated to explain the presence of $\text{C}_2\text{H}_3\text{S}^+$ in the dimethyl sulphide dimer cation photolysis²⁴ and rearrangement in the solvolysis of some *b*-thiovinyl sulphonates²⁵.

3.1c *Laser power dependence*: Results of laser energy dependence experiments for the integrated intensity of different ion signals in 355 nm photoionisation of DMS are shown in figure 2. For the parent ion ($m/e = 62$), the straight line fit to the experimental points gives a slope of (2 ± 0.2) (figure 2a). Since the ionization potential of CH_3SCH_3 is 8.69 eV¹⁷, the observed power dependence for the parent ion signal provides evidence for a two-photon resonant rate-determining absorption step followed by a saturated ionization step. The power dependence for CH_3S^+ (figure 2b), CH_2S^+ and $\text{CH}_3\text{SCH}_2^+$ (not shown) was also found to be ≈ 2 implying that these ions are produced by unimolecular fragmentation of the parent ion. However, HCS^+ ($m/e = 45$) and CH_3^+ ($m/e = 15$) show a laser power dependence of (3.5 ± 0.1) (figure 2c and d). In the case of DMDS photoionisation at 355 nm also we found similar power dependence of 4.1 ± 0.2 for $m/e = 45$ and 15.

It has been pointed out that the numbers obtained from power dependence experiments must be treated with caution since experimental conditions may play a major role in determining the apparent order of the process under study^{22,26}. However, different power dependences for different ions obtained from the same set of experiments do reflect a change in mechanism of their production. We report the power dependences of different ions and use them qualitatively to understand their origin.

The complex fragment ion mass spectra and their different laser power dependences indicate that more than one mechanism is operative in the photoionisation of DMS at 355 nm. In the visible and UV multiphoton dissociation/ionisation time-of-flight study of a

very similar compound, dimethyl selenide (CH_3SeCH_3 , DMSe), Belbruno *et al*²² suggested that there are two competitive ionisation channels. The first involves neutral dissociation of CH_3SeCH_3 followed by the ionisation of the fragments (dissociation followed by ionisation) and the second one proceeds by direct ionisation of CH_3SeCH_3 with its subsequent fragmentation (ionisation followed by dissociation).

The different power dependences for different fragment ions obtained in the present study, can be understood based on the two-photon excitation of molecules to an excited state ≈ 7 eV. Some of the molecules undergo dissociation whereas the others get ionised. Molecules in this excited state can absorb another photon and reach the ionisation level by a $(2 + 1)$ REMPI process. Such a scheme gives rise to a laser power dependence of two for the parent ion peak ($m/e = 62$) which has been experimentally observed. Other fractions of molecules which undergo dissociation from the 7 eV state, produce $\text{CH}_3\text{S}^\bullet$ in

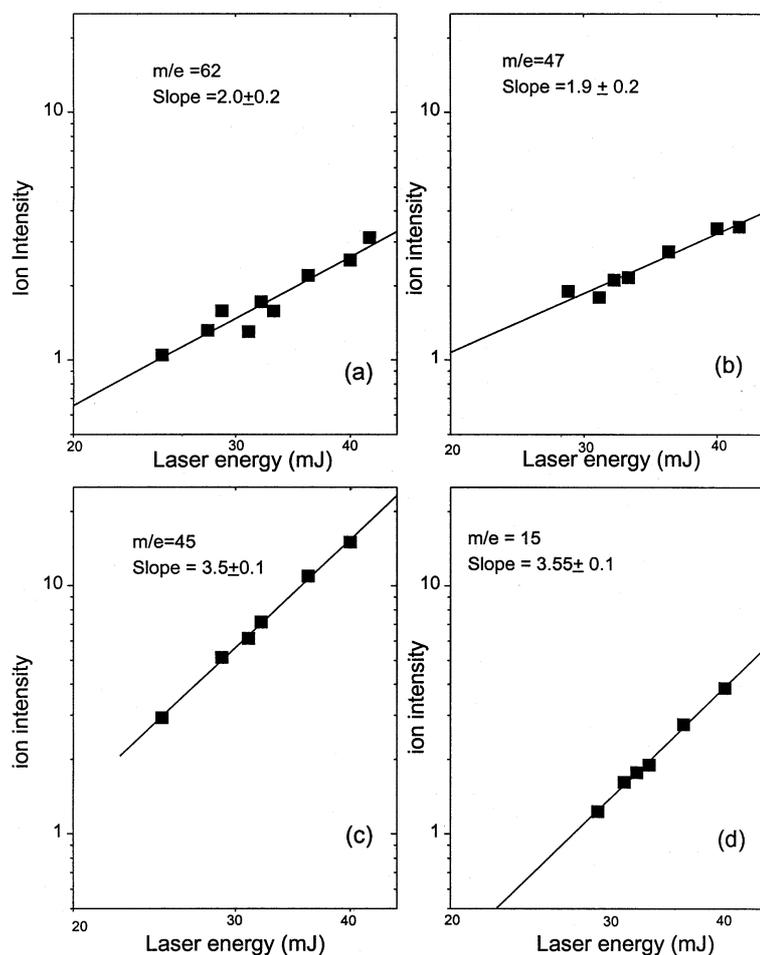
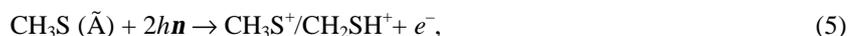
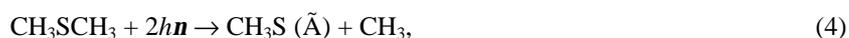


Figure 2. Log-log plot of laser energy vs ion intensity for DMS at 355 nm, $m/e = 62$ (a), 47 (b), 45 (c) and 15 (d).

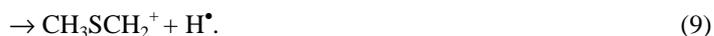
the \tilde{A} state¹³. Since the 0–0 transition of CH_3S radical is at 377 nm¹², the radical has an excess energy of at least 3.29 eV. These CH_3S radicals in the \tilde{A} state can be ionised by another two photons of 355 nm from the same laser pulse since the ionisation potential of CH_3S is 9.22 eV²⁷. CH_3S^+ produced by this mechanism has a minimum excess energy of 1.07 eV which is sufficient for it to isomerise into CH_2SH^+ . The barrier for isomerisation is 0.9 eV and CH_2SH^+ is more stable than CH_3S^+ by 1.3 eV²⁸. Thus, CH_2SH^+ is produced with total excess energy of 2.37 eV. For $\text{CH}_3\text{S}^+/\text{CH}_2\text{SH}^+$ it has been shown²⁸ that for an excess energy of 2 eV, the unimolecular dissociation rate into HCS^+ is of the order of 10^{10} – 10^{11} s⁻¹. Thus, $\text{CH}_3\text{S}^+/\text{CH}_2\text{SH}^+$ with such an amount of excess energy instantaneously decays into HCS^+ . The complete scheme for the formation of HCS^+ is shown below.



Since two photons are required for dissociation and another two for ionisation, this mechanism should have resulted in a power dependence of nearly four for CH_3S^+ , HCS^+ and CH_3^+ . Whereas HCS^+ and CH_3^+ show a power dependence of (3.5 ± 0.1) , the observed power dependence for CH_3S^+ is two, indicating that two types of CH_3S^+ are produced in these experiments, one via the (2 + 1) mechanism and other via the (2 + 2) mechanism. Those detected at $m/e = 47$ are mainly produced by the parent ion dissociation (2 + 1 mechanism) and have very little excess energy. The CH_3S^+ produced by molecular dissociation into $\text{CH}_3\text{S} + \text{CH}_3$ radicals followed by CH_3S ionisation mechanism are metastable and most of them undergo unimolecular dissociation to produce HCS^+ and H_2 . This is supported by the experiments at low intensity where the relative abundance of $m/e = 47/45$ increases reflecting the dominance of a (2 + 1) process over the (2 + 2) process.

It may be argued that absorption of one photon by the parent ion which then dissociates to give different products also results in four photon dependence. However, there is no excited state of the parent ion at 3.5 eV as shown by the photoelectron spectrum of the molecule¹⁸. Thus, the absorption of the fourth photon by the parent ion is unlikely suggesting that the origin of CH_3^+ and HCS^+ , which exhibit a power dependence of 3.5, cannot be through this mechanism.

3.1d *Dissociation of molecular ion:* In photoelectron–photoion coincidence (PEPICO) studies, Nourbakhsh *et al*⁹ have shown that the molecular ion is stable upto an energy of 10.4 eV after which it starts dissociating competitively as per the following three channels, producing ions of $m/e = 46, 47$ and 61.



Recent complete basis set *ab-initio* calculations²⁹ also showed that CH_3SCH_3 radical cation decomposition basically occurs through 1,2 hydrogen rearrangement from α -carbon to the sulphur atom followed by S–H or S–C bond breaking to produce $\text{CH}_3\text{SCH}_2^+$ ($m/e = 61$) or CH_2SH^+ ($m/e = 47$). It was further argued by Jursic²⁹ that two decomposition routes, namely, hydrogen or methyl radical elimination might coexist in the decomposition of CH_3SCH_3 radical cations because they are very close in energy. In the present experiments, the molecule after (2 + 1) REMPI process at 355 nm, has energy of 10.5 eV which is just above the threshold for dissociation at 10.4 eV. The two photon dependence for the molecular ion and for CH_3S^+ , CH_2S^+ and $\text{CH}_3\text{SCH}_2^+$ shows that these daughter fragments are produced by the unimolecular dissociation of CH_3SCH_3 radical cation. Thus, with respect to the dissociation of the molecular ion, the present results are in qualitative agreement with the PEPICO results of Nourbakhsh *et al*⁹ and with the computational studies of Jursic²⁹.

3.2 Photoionisation at 532 nm

In 532 nm photoionisation, the mass spectrum is similar to that at 355 nm but the parent ion signal ($m/e = 62$) could not be detected (figure 1c). However, the signals at $m/e = 61$ and $m/e = 35$ (SH_3^+) are more intense than that at 355 nm. In this case also, the major fragment ion is HCS^+ and the relative intensities of different mass peaks in $m/e = 44$ –47 region do not change appreciably with change in laser intensity.

The absence of a parent ion in the entire intensity range indicates that the laser intensity is not sufficient to excite the molecule up to the ionisation level. Since fragment ion signals are observed, it is apparent that the molecule is excited to a dissociative state which fragments into radical products that are subsequently ionised. The other possibility of molecular ion formation followed by its photodissociation by the laser field is ruled out in view of the fact that parent ion does not have absorption at 532 nm¹⁸. The mass spectrum shows that both dissociation channels, mentioned in (1) and (2) earlier operate. Radicals CH_3SCH_2 , CH_3S and CH_3 absorb additional photons from the same laser pulse and get ionised.

The C–S bond dissociation energy is 3.26 eV and the C–H bond energy is 3.95 eV⁸. Due to the higher threshold, the branching into H-atom elimination channel is expected to be less. Considering comparable ionisation efficiencies for the CH_3SCH_2 and CH_3S radicals, the signal owing to $\text{CH}_3\text{SCH}_2^+$ will therefore be less as compared to the signals due to $\text{CH}_3^+/\text{CH}_3\text{S}^+$, which is consistent with experimental observations (figure 1c). In principle the molecule can dissociate after absorbing either two or three photons at 532 nm. The results of three photon dissociation at 532 nm are expected to be qualitatively similar to that of two photon dissociation at 355 nm. However, the present results show that the relative intensities of different ion signals, particularly in the region of $m/e = 44$ to 47, is found to be different as can be seen from figure 1a and c. Thus, we are inclined to believe that the molecular dissociation at 532 nm occurs after absorption of two photons.

It is of interest to mention that the present multiphoton dissociation results appear to be in disagreement with the single photon dissociation results at 227.5 nm (5.43 eV) reported by Haya *et al*¹¹, where only C–S bond breaking was reported and not C–H although the photon energy was sufficient to break both the bonds. The reason for this apparent difference is that in the study of Haya *et al*¹¹, the probe laser was tuned to (2 + 1) REMPI transition of CH_3 radicals at 286.3 nm and did not probe other dissociation products.

4. Conclusion

In conclusion, we have presented the results of multiphoton excitation/ionization on CH_3SCH_3 following excitation at 355 and 532 nm. In the case of 355 nm excitation, a parent ion could be observed which showed a laser power dependence of two. Some of the parent ions dissociate competitively into various product channels producing CH_2S^+ , CH_3S^+ and $\text{CH}_3\text{CH}_2\text{S}^+$. Ion signals at $m/e = 46, 47$ and 61 show two-photon laser power dependence suggesting that they arise from the dissociation of molecular ions. Ion signals at $m/e = 15$ and 45 show four-photon dependence and have been proposed to originate from dissociation of the neutral molecules followed by ionisation of the fragment radicals. It has been observed that above a certain energy CH_3S^+ undergoes unimolecular dissociation into $\text{HCS}^+ + \text{H}_2$ in agreement with theoretical predictions. At 532 nm, however, no parent ion could be observed and only ions of dissociated radical products were detected. SH_3^+ has been suggested to originate from $\text{CH}_3\text{SCH}_2^+$ via a cyclic transition state.

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