

# MULTIPHOTON IONIZATION AND FRAGMENTATION OF CS<sub>2</sub> UNDER INTENSE SHORT PULSE LASER RADIATION

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The interaction of CS<sub>2</sub> with intense short pulse laser radiation is studied experimentally using time-of-flight mass spectroscopy. Laser pulses of 0.5 and 5 psec at 248 and 496 nm have been used in order to investigate the effect of the wavelength and the pulse duration on the molecular ionization and fragmentation. As shown, for low enough intensities the parent molecular ion is present as the most important peak in all cases. Increasing the intensity results in extensive fragmentation, where the molecular parent ion remains always the more intense mass peak at 496 nm while at 248 nm S<sup>+</sup> dominates the mass spectra. Finally, the production of multiply charged fragments is more efficient at the longer wavelength used.

*Keywords:* Multiphoton ionization/fragmentation; CS<sub>2</sub>; time-of-flight mass spectroscopy; multiple charged ions; short pulse laser-molecule interactions

## INTRODUCTION

The study of ionization, dissociation and/or fragmentation of molecules in the gas phase under irradiation with short laser pulses has received a lot of interest during the last few years, especially since the technology of femto-second (fsec) laser systems became readily available. As a result significant information has been revealed towards the understanding of elementary and fundamental physical and chemical processes [1].

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Although the use of short laser pulses and high intensities has stimulated intense research interest in the field of molecular fragmentation and dynamics, a lot of questions still remain open, not only due to the lack of appropriate theory but also due to the fragmented and sometimes controversial experimental results appearing in the literature.

The motivation of the present work is to provide a consistent set of data on the multiphoton ionization and fragmentation of a simple and well studied, from the spectroscopic point of view, small molecule like CS<sub>2</sub>, using different laser pulse durations and wavelengths. The experimental results presented here are consistent in the sense that they have been obtained under the same experimental conditions, changing only the characteristics of the laser excitation. The main question that we are addressing here is the competition between ionization and fragmentation *i.e.*, if the molecule ionizes first and then dissociates or vice versa and what ionization/fragmentation channels are favored depending on the pulse duration and the wavelength used. These questions are investigated here for intensities ranging between 10<sup>9</sup> and 4 × 10<sup>12</sup> W/cm<sup>2</sup>. More work is currently underway in order to extend the range of intensities up to 10<sup>16</sup> W/cm<sup>2</sup>.

## EXPERIMENTAL

The laser system employed here is a hybrid excimer-dye laser system based on the concept of distributed feedback dye laser (DFDL). Specifically, the 308 nm (XeCl) output of a double-cavity excimer laser (Lambda Physik EMG 150 MSC) pumps a cascade of dye laser modules to produce 0.5 psec pulses at 496 nm with a corresponding energy of 100 μJ. This seeding pulse is frequency doubled in a BBO crystal and amplified in a double pass by a KrF second cavity of the excimer unit. The resulting UV laser beam at 248 nm has a pulse duration of 500 fsec, a repetition rate up to 20 Hz and a maximum energy of 20 mJ per pulse. By inserting a bandwidth limiting etalon pulses 5 psec long at both 496 and 248 nm can be produced. Laser pulse diagnostics are obtained on-line by a 1m Littrow-type spectrograph and a multiple shot autocorrelator at 248 nm. Attention was paid to clean operation of the system in providing low amplified spontaneous emission (ASE) content in the laser output, which is monitored both by energy measurements of

ASE *versus* total energy in the near field, and through the autocorrelation profile having the correct signal-total background ratio.

The nanosecond laser system used was a Lambda Physik FL2001 dye laser pumped by a Lambda Physik 201 MSC excimer laser operating at 308 nm. The tunable laser light has a bandwidth of  $0.3\text{ cm}^{-1}$ , duration of 15 nsec and provides energies of several mJ.

A home made time-of-flight mass spectrometer has been used, consisting of a 60 cm long field-free drift tube and an extracting electrode arrangement of a repeller plate (+1900 V) and a guarding electrode (grounded) separated by 1.5 cm. Unit mass-resolved cation signals were detected by a pair of 2.5 cm diameter channel plates. Alternatively, another 100 cm long Wiley-McLaren type time-of-flight was employed, having an electrode arrangement consisting of a repeller plate (at +1900 V) and an acceleration plate (at +1500V) followed by a grounded electrode. The distance between the electrodes was 2 cm. From the extracted ions, only those that were passing through a 1 mm pinhole placed on the geometrical axis of the field-free tube were allowed to reach the detector. A mixture of 50 mbar CS<sub>2</sub> in 200 mbar argon was expanded through a 0.3 mm nozzle into the vacuum chamber. The pressure in the chamber was always kept below  $10^{-6}$  mbar during the recording of the mass spectra. Spectroscopic grade CS<sub>2</sub> was used after several repeated freeze-thaw-degassing cycles under vacuum.

The laser beam was focused by means of plano-convex quartz lens, of 15 cm focal length and in the case of the short pulses at 248 nm only the central part of the beam was utilized passing through an aperture. In addition, the polarization was set parallel to the TOF axis for all the experiments presented here. Special care was taken to insure that no space-charge effects would perturb the mass spectra measurements. A previously calibrated Molectron J4-09 energy meter measured the energy of the laser beam. The beam diameter was measured at the focus using a linear diode array and was found to be 40  $\mu\text{m}$  and 25  $\mu\text{m}$  at 496 and 248 nm, respectively.

## RESULTS AND DISCUSSION

Mass spectra have been recorded under several experimental conditions, at both wavelengths and pulse durations used. Each mass spectrum

presented here is the average of the corresponding mass spectra of 100 to 500 laser shots and is normalized with respect to the  $\text{CS}_2^+$  mass peak for comparison purposes. Absolute signals can be obtained by dividing the presented spectra by the appropriate factors indicated in each figure. In Figure 1, we present mass spectra that have been recorded at the lowest possible laser energies used with our experimental setup for which a signal can be recorded. As is shown in all cases, the more intense peak of the spectra is the one corresponding to  $\text{CS}_2^+$  ( $m/q = 76$ ), the molecular parent ion. Moreover, the presence of the  $\text{S}^+$  ( $m/q = 32$ ) and  $\text{CS}^+$  ( $m/q = 44$ ) mass peaks, even though smaller in intensity, is evident even at the lowest intensities employed for all cases, their contribution being relatively more important at 248 nm and for 5 psec pulses. All sulfur-containing ions were accompanied by a small peak corresponding to the  $^{34}\text{S}$  isotope, which has a natural abundance of 4%.

The fragmentation pattern changes dramatically at higher intensities, as depicted in Figure 2, where extensive fragmentation is observed in all cases. However, comparing the mass spectra obtained with the

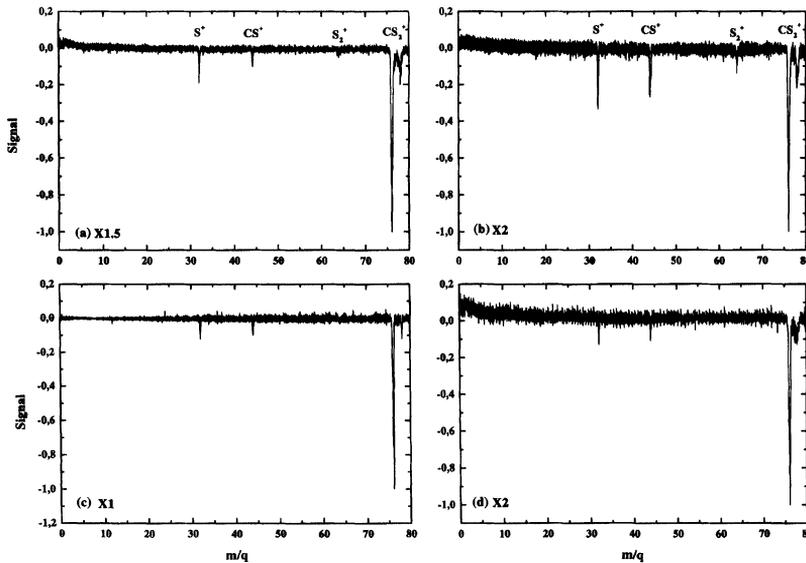


FIGURE 1 Typical mass spectra of  $\text{CS}_2$  at low incident intensities corresponding to: (a) 248 nm, 0.5 psec,  $I = 6.7 \times 10^9 \text{ W/cm}^2$ , (b) 248 nm, 5 psec,  $I = 2 \times 10^9 \text{ W/cm}^2$ , (c) 496 nm, 0.5 psec,  $I = 1.5 \times 10^{11} \text{ W/cm}^2$  and (d) 496 nm, 5 psec,  $I = 9 \times 10^{10} \text{ W/cm}^2$ .

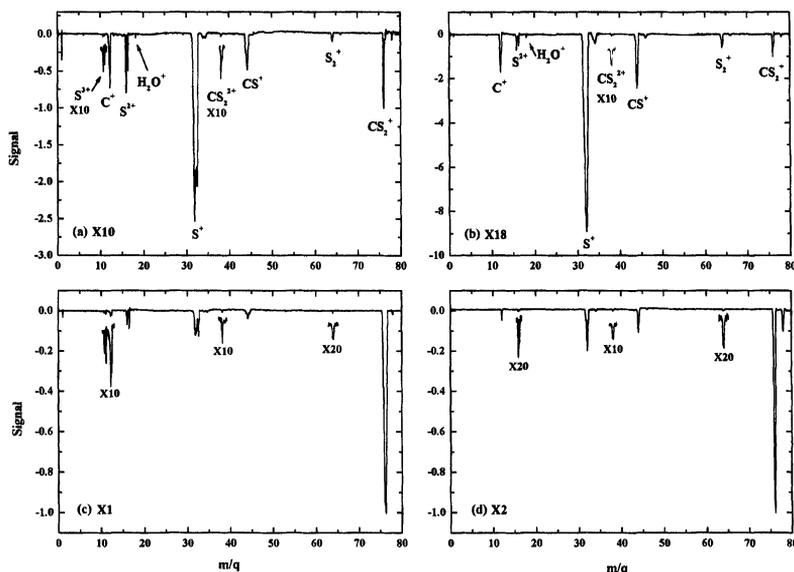


FIGURE 2 Typical mass spectra of CS<sub>2</sub> at high incident intensities corresponding to: (a) 248 nm, 0.5 psec,  $I = 1.5 \times 10^{12}$  W/cm<sup>2</sup>, (b) 248 nm, 5 psec,  $I = 1.8 \times 10^{11}$  W/cm<sup>2</sup>, (c) 496 nm, 0.5 psec,  $I = 1.5 \times 10^{12}$  W/cm<sup>2</sup> and (d) 496 nm, 5 psec,  $I = 1.8 \times 10^{11}$  W/cm<sup>2</sup>.

same pulse duration and with similar incident laser intensities, the parent molecular ion remained the most prominent mass peak at 496 nm, while at 248 nm, the sulfur ion dominated the spectra. The CS<sup>+</sup> and C<sup>+</sup> ( $m/q = 12$ ) ions were also present in all cases, being in general relatively more important at 248 nm. Appreciable quantities of S<sup>2+</sup> ( $m/q = 16$ ) were also observed for both wavelengths and pulse durations used. Small signals of S<sup>3+</sup> ( $m/q = 10.67$ ) and S<sub>2</sub><sup>+</sup> ( $m/q = 64$ ) were present, the former being more intense at 496 and the latter at 248 nm respectively. Furthermore, in the mass spectra at both wavelengths, small intensity signals corresponding to the doubly ionized parent molecular ion CS<sub>2</sub><sup>2+</sup> ( $m/q = 38$ ) and C<sup>2+</sup> ( $m/q = 6$ ) have also been observed. In addition, at even higher intensities, S<sup>4+</sup> ( $m/q = 8$ ) was observed at 496 nm, 0.5 psec. It has to be noted that at the high intensities used, the S<sup>+</sup> and all the multiple charged fragments (S<sup>2+</sup>, S<sup>3+</sup>, S<sup>4+</sup>, C<sup>2+</sup>) exhibit significant splitting most probably due to Coulomb explosion. Finally, at 248 nm, the presence of H<sub>2</sub>O<sup>+</sup> ( $m/q = 18$ ) was also clearly distinguishable, being more important for the shorter

duration pulses. The appearance of  $\text{H}_2\text{O}^+$  is most probably due to humidity present in our TOF system, the gas handling apparatus, water traces present in the  $\text{CS}_2$ , or the carrier gas used. The water signature was found to always be present at shorter wavelengths and appears at longer wavelengths only when high enough intensities were employed.

In Figures 3a,b and 4a,b, we present the evolution of the ratio of the signal (*i.e.*, the integrated area of the respective mass peaks) for each principle fragment observed ( $\text{S}^+$ ,  $\text{CS}^+$  and  $\text{C}^+$ ), divided by the corresponding signal of the molecular parent ion, at the range of intensities used. Comparing the values of the ratio of the fragment to the parent molecular ion, it is evident that at 496 nm (Figures 3a and b),  $\text{CS}_2^+$  is the most important peak in all the spectra recorded, the ratio exhibiting values always smaller than one, for both pulse durations. The reduction of the ratio occurring at high intensities is related to the fact that the parent ion signal continuously increases within the intensity range used, while the fragments tend to saturate earlier. In addition, at such intensities, the presence of multiply charged fragments becomes significant.

The fragmentation pattern observed here is not in agreement with what has been previously reported [2–5], where the second harmonic (532 nm) of a 35 psec Nd:YAG has been used as the laser excitation source. In these experiments, the relative intensities of  $\text{S}^+$ ,  $\text{C}^+$  and  $\text{CS}_2^+$  have been measured at laser intensities similar to the ones used in the present work. As shown in Figures 3 and 5 of Refs. [1] and [2] respectively, their mass spectra differ significantly from ours since, in their case  $\text{S}^+$  is the major mass peak at low intensity and only at high intensity the  $\text{CS}_2^+$  peak becomes important. A possible reason for this discrepancy may be the longer pulses used in Refs. [1, 2].

Under 248 nm excitation (Figure 4a and b), the principal fragments  $\text{S}^+$ ,  $\text{CS}^+$  and  $\text{C}^+$ , were found to be more intense or at least of comparable intensity to the parent ion peak, for both pulse durations used, the effect being more pronounced at 5 psec. This observation is in partial agreement with the results presented in Figure 2 of Ref. [3], where the third harmonic (355 nm) of a 35 psec Nd:YAG laser was employed. In these results, the parent ion was found to be much less abundant than the fragment ions, a behavior similar to what we have observed at high intensities. However, it must be pointed out that in our results and at low incident intensities,  $\text{CS}_2^+$  was found to be the most

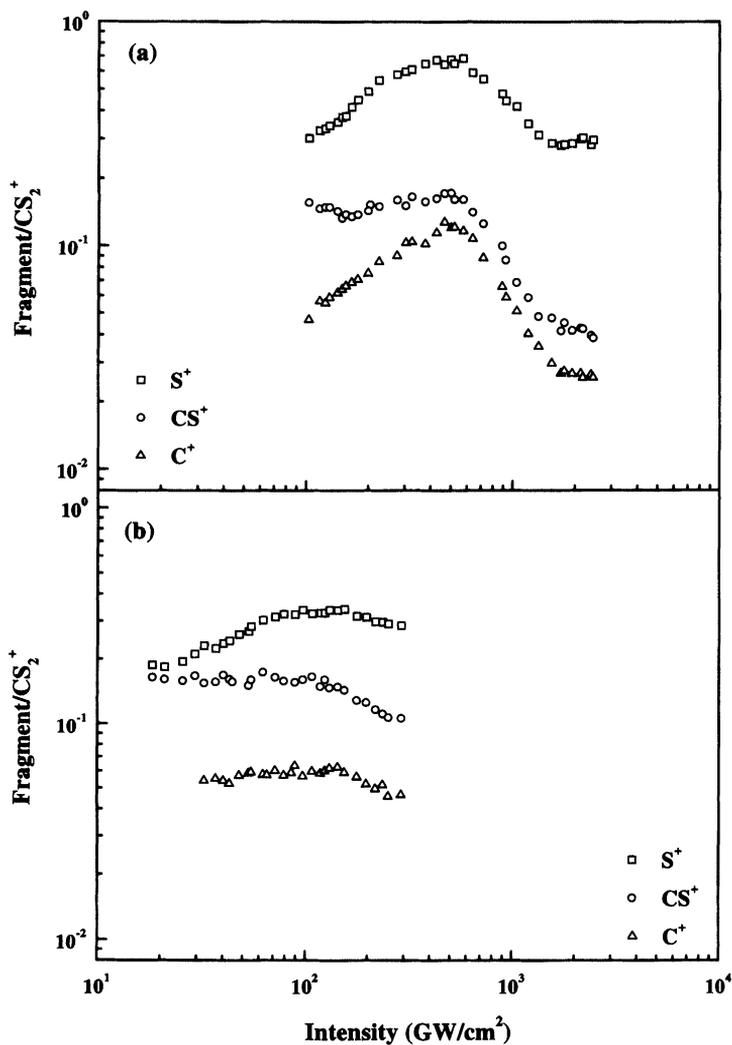


FIGURE 3 Variation of the ratio of the signal of the principal fragments ( $S^+$ ,  $CS^+$ ,  $C^+$ ) over the signal of the parent molecular ion ( $CS_2^+$ ) as a function of the incident laser intensity at 496 nm for: (a) 0.5 psec and (b) 5 psec laser pulses.

important feature of the mass spectra, while in Ref. [3] no significant difference had been observed between 532 and 355 nm.

In Figure 5, we present the ratio of the signal corresponding to the sum of all fragments (except  $CS_2^+$ ) over the  $CS_2^+$  signal. As shown, at

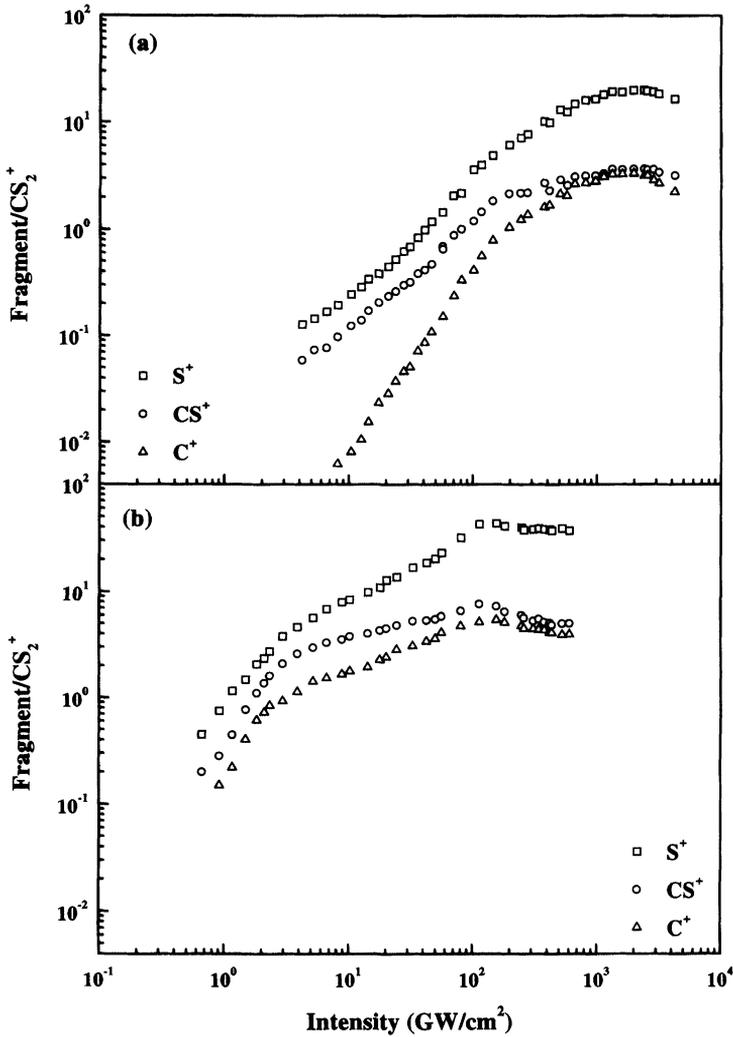


FIGURE 4 Variation of the ratio of the signal of the principal fragments ( $S^+$ ,  $CS^+$ ,  $C^+$ ) over the signal of the parent molecular ion ( $CS_2^+$ ) as a function of the incident laser intensity at 248 nm for: (a) 0.5 psec and (b) 5 psec laser pulses.

248 nm the ratio smoothly increases, largely exceeding the value of one, while at 496 nm it is constantly smaller than one and decreases with intensity. It is noteworthy that at low incident intensities for both pulse durations at 248 nm, the ratio approaches unity, its value becoming

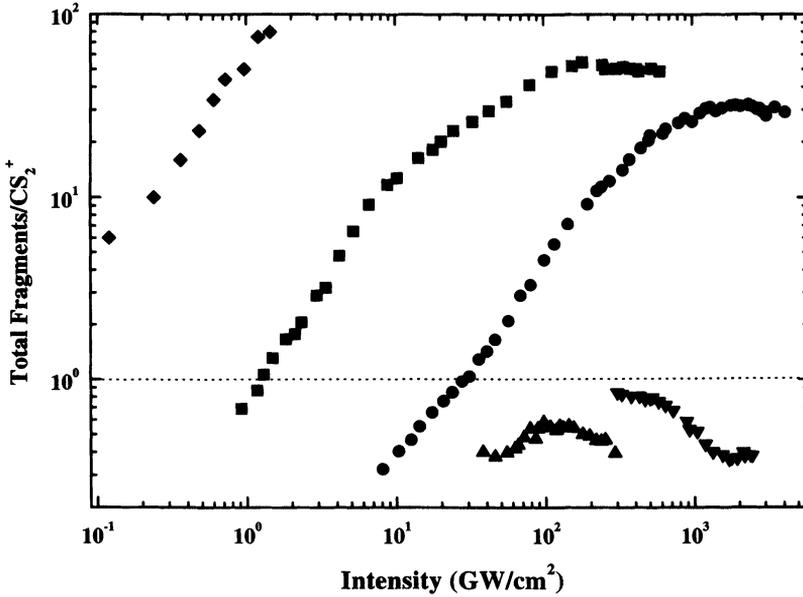


FIGURE 5 Variation of the ratio of the total ion signal (all fragments except CS<sub>2</sub><sup>+</sup>) over the signal of the parent molecular ion (CS<sub>2</sub><sup>+</sup>) as a function of the incident laser intensity for: (a) 248 nm, 0.5 psec (●), (b) 248 nm, 5 psec (■), (c) 496 nm, 0.5 psec (▼), (d) 496 nm, 5 psec (▲) (e) 248 nm, 15 nsec (◆).

larger for 5 psec ( $\sim 60$ ) than for 0.5 psec ( $\sim 30$ ) at higher intensities. The increase of the ratio is even more pronounced for 15 nsec pulses, where the ratio attains values two orders of magnitude larger than those obtained at 5 psec, 248 nm. The physical insight of Figure 5 is that shorter wavelengths tend to fragment the molecule more efficiently, while longer wavelengths result in reduced fragmentation and more parent ion production. Also, at the same wavelength, the fragmentation is more efficient for longer pulses. Preliminary experiments currently underway, using 800 and 400 nm laser pulses of 200 fsec and 50 fsec duration, confirm again that longer wavelengths and shorter pulses favor the formation of the molecular parent ion, while shorter wavelengths result in enhanced fragmentation. This is consistent with what has been previously reported in Ref. [6], where the multiphoton multi-electron dissociative ionization of CO at two wavelengths, 305 and 610 nm have been studied.

Considering the above experimental results and the low intensity mass spectra of Figure 1, it is irrefutable that the parent molecular ion is produced in considerable amounts and reduced fragmentation is observed at both wavelengths and pulse durations at relatively low intensities. Taking into account the ionization potential (I.P.) of CS<sub>2</sub> [7] (Tab. I), the molecule must absorb at least 3 and 5 photons at 248 and 496 nm respectively, in order to be ionized. In the former case, the absorption of three photons corresponding to an energy of 15 eV, brings the molecule slightly above the dissociation limit of the  $\tilde{B}^2\Sigma_u^+$  state of the molecular ion, leading to S<sup>+</sup>(<sup>4</sup>S) and CS(<sup>1</sup>Σ<sup>+</sup>) (the threshold limit being at 14.81 eV [8]). This implies that S<sup>+</sup> will be inevitably produced when the molecule is ionized. Moreover, sulfur atoms, having an ionization potential of 10.35 eV [9], can be also easily ionized at these intensities, resulting in enhanced S<sup>+</sup> production. This is nicely depicted in Figures 4a and b, where the ratio S<sup>+</sup>/CS<sub>2</sub><sup>+</sup> increases with incident intensity, approaching the value of 20 and 40 for 0.5 and 5 psec pulses respectively. Meanwhile, the produced neutral CS(<sup>1</sup>Σ<sup>+</sup>) can also absorb three 248-photon [10] (Tab. I) becoming ionized within the laser pulse. Similarly, at the 4-photon level, corresponding to 20 eV, CS<sup>+</sup> and S<sub>2</sub><sup>+</sup> can be efficiently produced [7]. The intensity dependence of the principal fragments and the parent ion and their saturation appearing in the order CS<sub>2</sub><sup>+</sup>, S<sup>+</sup>, CS<sup>+</sup> and C<sup>+</sup>, also support the previous picture. Increasing the intensity of the incident laser radiation, more channels can be reached through the absorption of more photons and consequent fragmentation of the produced molecular ions and/or during the fragmentation of the multiply charged CS<sub>2</sub><sup>q+</sup> ( $q \geq 1$ ) ions. In this respect, CS<sub>2</sub><sup>+</sup> (after absorption of 3 or more 248 nm photons

TABLE I Appearance potentials of atomic and molecular species of interest

<i>Species</i>	<i>I. P. (eV)</i>	<i>Reference</i>
CS <sub>2</sub> <sup>+</sup>	10.08	[7]
CS <sub>2</sub> <sup>2+</sup>	27.3	[11]
CS <sup>+</sup>	11.33	[10]
S <sup>+</sup>	10.36	[9]
S <sup>2+</sup>	23.34	[9]
S <sup>3+</sup>	34.79	[9]
S <sup>4+</sup>	47.22	[9]
C <sup>+</sup>	11.26	[9]
C <sup>2+</sup>	24.37	[9]
S <sub>2</sub> <sup>+</sup>	9.35	[13]

by the neutral molecule) and CS<sub>2</sub><sup>2+</sup> can be seriously considered as precursors towards the production of the S<sup>q+</sup> and C<sup>q+</sup> ( $q \geq 1$ ) [5].

In the case of 496 nm photons, the molecule has to absorb at least 5 photons to be ionized, corresponding to an energy of 12.47 eV. The intensity dependence of the ion signals reveals that the saturation regime of the principal fragments is reached almost simultaneously by all of them, the CS<sub>2</sub><sup>+</sup> saturating at higher intensities and remaining the most important peak in all cases. Moreover, the production of the doubly charged parent ion CS<sub>2</sub><sup>2+</sup> [11] and multiply charged fragments, *i.e.*, S<sup>2+</sup>, S<sup>3+</sup>, S<sup>4+</sup> and C<sup>2+</sup> [9] (see also Tab. I) occur with relatively large yields compared to the parent ion and at least larger than the value at shorter wavelengths.

In Figure 6, the ratio of the S<sup>2+</sup> and S<sup>3+</sup> signals over the S<sup>+</sup> signal at 496 and 248 nm is shown for 0.5 psec duration pulses. As depicted, the S<sup>2+</sup> ions appear at lower intensity at 248 nm than at 496 nm, a behavior consistent with the concept of a multiphoton process, where the number of photons required for the ionization at 248 nm is half of that needed at 496 nm. On the other hand, the S<sup>3+</sup> ions seem to be produced at the

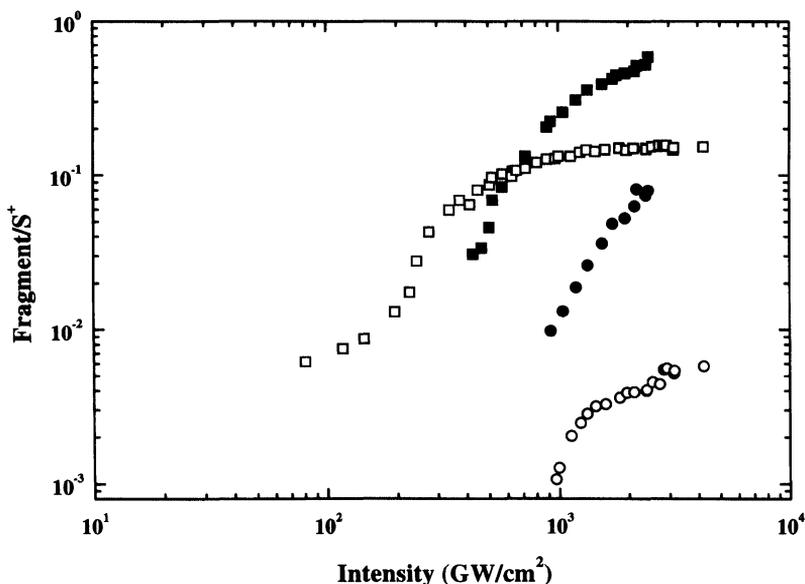


FIGURE 6 Ratios of S<sup>2+</sup>/S<sup>+</sup> (squares) and S<sup>3+</sup>/S<sup>+</sup> (circles) *versus* incident laser intensity at 496 nm (filled symbols) and 248 nm (open symbols) for 0.5 psec pulses.

same intensity of  $10^{12}$  W/cm<sup>2</sup> at both wavelengths. This should most probably reflect the different mechanism responsible for their production. The ratio of S<sup>2+</sup>/S<sup>+</sup> at 248 nm increases with intensity at the beginning, reaching rapidly a saturation regime, where the S<sup>3+</sup> ion signal appears which in turn exhibits saturation at an intensity of  $4 \times 10^{12}$  W/cm<sup>2</sup>. At the longer wavelength of 496 nm, the ratio S<sup>2+</sup>/S<sup>+</sup> increases continuously and even more rapidly than at 248 nm, never reaching saturation (for the intensities used) and exhibits values even larger than those at 248 nm. Similar behavior is seen for the S<sup>3+</sup>/S<sup>+</sup> ratio at 496 nm, that attains almost the same saturation value of the S<sup>2+</sup>/S<sup>+</sup> ratio at 248 nm. These observations strongly indicate that at the shorter wavelengths used the production of the principle fragments is favored in contrast to the longer wavelength, where multiply charged fragments are more efficiently produced.

The dynamics of the laser light-molecule interaction is often characterized by taking into account the adiabatic Keldysh [11] parameter  $\gamma$ , which provides an indication whether the ionization process takes place in the multiphoton or in the field ionization regime. Moreover its value, with a dependence on the wavelength  $\lambda$  (in  $\mu\text{m}$ ), the intensity of the incident light  $I$  (in W/cm<sup>2</sup>) and the ionization potential  $E_i$  (in eV), is given by the following relation:  $\gamma = \sqrt{E_i / (1.87 \times 10^{-13} I \lambda^2)}$ . When  $\gamma \gg 1$ , multiphoton processes are the dominant mechanism for the ionization of the molecule. When  $\gamma \ll 1$ , then field ionization explains better the ionization. For  $\gamma$  values near 1, an intermediate mechanism is generally assumed. By substituting in the formula the parameters that correspond to our experimental conditions, we found that the lowest  $\gamma$  values, corresponding to the highest intensities used, were 10 and 16 for 496 and 248 nm respectively. These values being much larger than one indicate that we are operating at the multiphoton regime.

Another interesting point is the presence of the S<sub>2</sub><sup>+</sup> mass peak [13] (Tab. I) and its dependence on the wavelength and the pulse duration. As shown in Figure 7, shorter wavelength and longer pulses enhanced the formation of S<sub>2</sub><sup>+</sup>. In particular, while at 496 nm the ratio S<sub>2</sub><sup>+</sup>/CS<sub>2</sub><sup>+</sup> was found continuously decreasing with intensity, at 248 nm it was slightly increasing and reached a plateau for both 0.5 and 5 psec. This behavior appears to be even more pronounced when the same wavelength but 15 nsec duration laser pulses were employed, the ratio exhibiting an almost tenfold increase. The observation of the formation of

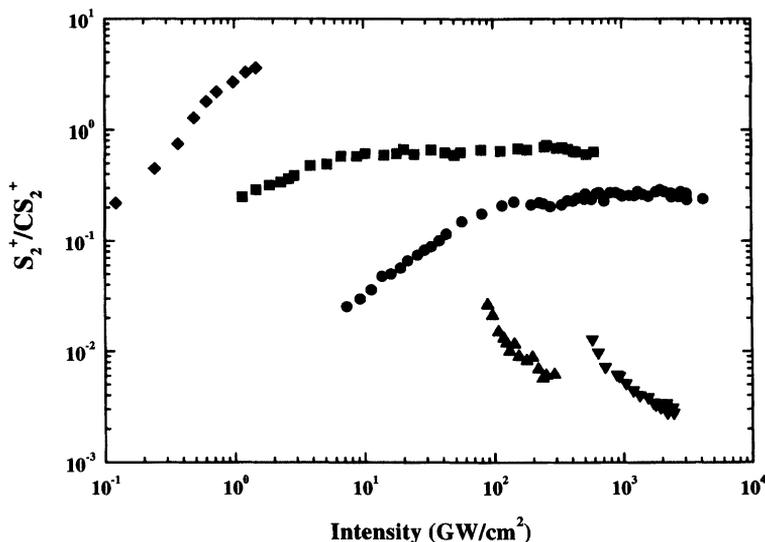


FIGURE 7 Ratio of  $S_2^+/CS_2^+$  as a function of the incident laser intensity for: (a) 248 nm, 0.5 psec ( $\bullet$ ), (b) 248 nm, 5 psec ( $\blacksquare$ ), (c) 496 nm, 0.5 psec ( $\blacktriangledown$ ), (d) 496 nm, 5 psec ( $\blacktriangle$ ) (e) 248 nm, 15 nsec ( $\blacklozenge$ ).

$S_2^+$  in our experiments contradicts what has been previously reported in Refs. [2, 4, 5], where  $S_2^+$  was observed only in collisions of charged particles (*i.e.*, electrons, positive or negative ions) with CS<sub>2</sub> [4]. In Ref. [14], an explanation of the  $S_2^+$  formation was given, assuming the fragmentation of the CS<sub>2</sub><sup>+</sup> and CS<sub>2</sub><sup>2+</sup> ions through bent geometry states. Although this mechanism may be probable we believe that it is not very satisfactory, since we have observed  $S_2^+$  formation also using 400 and 800 nm, 200 fsec laser pulses. The fact that the dimer ion is formed at four different wavelengths does not favor the argument of potential resonances with bent states. This was also confirmed in studies of the Rydberg states of CS<sub>2</sub>, where  $S_2^+$  was observed at several wavelengths using nsec lasers [15–17].

## CONCLUSIONS

Experimental results were presented related to the interaction of CS<sub>2</sub> with intense short pulse laser radiation. It has been shown that when

short pulses are employed, the parent ion is the most important mass peak at low incident intensities, independently of the wavelength used. This implies that CS<sub>2</sub> first ionizes and then dissociates at the wavelengths, pulse durations and intensities used in this study. At higher intensities, at 248 nm, extended fragmentation was observed, S<sup>+</sup> being the major feature of the mass spectra, while at 496 nm, the ionization of the parent molecule was found to be more efficient. The production of multiply charged fragments was found enhanced at 496 nm. Finally, the formation of S<sub>2</sub><sup>+</sup> was enhanced at 248 nm.

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