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On the detection of higher order carbon sulfides (CS_x ; $x = 4-6$) in low temperature carbon disulfide ices

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7 **Low Temperature Carbon Disulfide Ices**

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Abstract

Higher-order carbon sulfides - carbon tetrasulfide (CS_4 ; D_{2d}), carbon pentasulfide (CS_5 ; C_2), and carbon hexasulfide (CS_6 , C_2) - were detected for the first time via infrared spectroscopy in low temperature carbon disulfide (CS_2) ices upon irradiation with energetic electrons. The identification of these molecules was aided via observed band positions of their C-12 and C-13 isotopologues and the agreement with vibrational modes and isotope shifts predicted from *ab initio* calculations. Reaction pathways to these species are discussed as well.

1. Introduction

During the last decades, experimental and theoretical studies on high-energy metastable compounds (HEMC) have drawn considerable interest. The decomposition of HEMC molecules is accompanied by the release of excessive energies up to 1000 kJ mol^{-1} , which makes this class of molecules attractive to future defense and space science application (explosives) [1-4]. More recently, the formation mechanisms of cyclic carbon oxides of the formula CO_x ($x=3-6$) were explored extensively (Figure 1) [5-12]. Carbon oxides are considered as prototype HEMCs, since they maintain a high oxygen balance and the decomposition of these molecules is strongly exoergic by 518 kJ mol^{-1} (for CO_6) [12-15]. However, the isovalent sulfur compounds carbon trisulfide (CS_3), carbon tetrasulfide (CS_4), carbon pentasulfide (CS_5) and carbon hexasulfide (CS_6) have not gained much attention to date. As a matter of fact, with the exception of carbon trisulfide (CS_3), higher order sulfides (CS_4 , CS_5 , CS_6) have eluded synthesis to date.

Apart from the identification, structural investigation, and reaction pathways to carbon sulfides, carbon sulfur clusters have also drawn considerable attentions from the interstellar chemistry and material science communities [16-20]. Carbon disulfide (CS_2) and small carbon sulfur clusters such as C_nS and C_nS_m ($n=1-3$, $m=1-2$) have attracted significant interest from the planetary science community, when fragments of comet Schoemaker-Levy 9 (SL-9) collided with Jupiter, and carbon-sulfur bearing molecules were detected [21]. In the laboratory, matrix isolation techniques have been exploited to trap and to produce carbon sulfur clusters. Pyrolysis and ultra violet (UV) photolysis of organo-sulfur precursors followed by trapping in an argon matrix led to the detection of dicarbon disulfide (C_2S_2) and carbon subsulfide (C_3S_2) [22-25]. Further, Bohn et al. utilized matrix isolation to trap high voltage discharge products of a carbon disulfide – argon gas mixture and characterized C_2S_2 and C_3S_2 molecule as well [26]. A series of small carbon sulfur clusters (C_nS ($n=1-7$) and C_mS_2 ($m=1-15$)) were identified by Vala et al. via infrared spectroscopy of laser ablated pressed graphite-sulfur mixture [27,28]. Further, reports on the computational investigation of structures of C_nS ($n=2,6$) and C_nS_2 ($n=2,6$) are also present [27, 29, 30].

With respect to higher carbon sulfide species, the synthesis of carbon trisulfide (CS_3) was first proposed by Basco et al. in 1967 via the gas phase reaction of ground state sulfur atoms ($\text{S}(^3\text{P}_j)$) with carbon disulfide (CS_2) in presence of an inert gas bath [31]. Engelke et al. as well as

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4 Sulzle et al. confirmed the formation of carbon trisulfide via mass spectroscopy [32, 33]. Fueled
5 by these experiments, Froese et al. conducted electronic structure calculations and suggested that
6 three isomers may exist: carbon trisulfide in C_{2v} and D_{3h} geometries as well as a bent, C_s -
7 symmetric SCSS isomer [34]. A recent infrared spectroscopic study by Ma et al. identified the
8 C_{2v} and C_s -symmetric carbon trisulfide isomers in an argon matrix; high level *ab initio*
9 calculations revealed that C_{2v} -symmetric carbon trisulfide isomer presents the global energy
10 minimum [35, 36]. Here, the molecular structure of the cyclic C_{2v} symmetric carbon trisulfide is
11 similar to the isovalent C_{2v} structure of the cyclic carbon trioxide (CO_3) molecule [5]. Note that
12 the D_{3h} symmetric CO_3 isomer was also identified, whereas the isovalent CS_3 isomer was not
13 confirmed experimentally [5, 35]. The molecular structures of CS_4 and CS_5 were investigated
14 computationally using B3LYP/6-311G* level of theory [37]. The study revealed that the
15 structure of CS_4 can be characterized as a van-der-Waals complex of CS_2 with S_2 , in which the
16 sulfur-sulfur distance between CS_2 and S_2 moiety was 4.358 Å. The molecular structure of CS_4
17 was distinctly different from its isovalent carbon tetraoxide (CO_4 ; C_{2v}) molecule (Figure 1) [6].
18 Similarly, the structure reported for of CS_5 (C_{2v}) was characterized by $S_2C(S)S_2$ which was
19 distinctly different from the carbon pentaoxide (CO_5) (C_2) structure [7]. Note that the existence
20 of sulfur chains (S_n) were reported in single crystal structure of carbon-sulfur clusters C_3S_8 and
21 C_6S_{12} [38].

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38 In this *Letter*, we present the first experimental detection of three higher carbon sulfides -
39 CS_4 (D_{2d}), CS_5 (C_2), and CS_6 (C_2) - formed via electron irradiation of low temperature carbon
40 disulfide ices at 12 K. The infrared spectroscopic detection of the CS_x ($x = 4-6$) species is
41 supported by isotopic substitution experiments ($C-12$ versus $C-13$) and with theoretically
42 expected isotope shifts.
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47 2. Experimental Methods

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The experiments were carried out in a contamination-free ultra high vacuum (UHV) chamber
at base pressures of 5×10^{-11} Torr [5-8, 10, 11]. A polished silver crystal interfaced to a two-stage
closed-cycle helium refrigerator was suspended on a rotary platform and situated in the center of
the main chamber. The silver crystal was cooled to 12 K and acted as a substrate for carbon
disulfide ices. Vapor of carbon disulfide ($^{12}CS_2$, Acros Organics, 99.9%; $^{13}CS_2$, Cambridge
Isotope Lab, 97-99 atom ^{13}C %) was introduced into the main chamber at pressures of 1.2×10^{-7}

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4 Torr via a precision leak valve and a glass capillary array and condensed on the cooled substrate
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6 for 10 minutes. This yielded carbon disulfide ice films with thicknesses of 300 ± 8 nm [5].
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9 The ice sample was then irradiated isothermally at 12 K with 5 keV electrons generated by an
10 electron gun (SPECS; EQ 22/35) at a nominal beam current of 0 (blank) 100 nA, 1000 nA, and
11 5000 nA over an area of 3.0 ± 0.2 cm². The radiation-induced chemical reactions in the ices
12 were monitored on line and in situ by a Nicolet Infrared Spectrometer (Nicolet 6700) in a
13 spectral range of 6000 to 500 cm⁻¹. Each FTIR spectrum was recorded in absorption-reflection-
14 absorption mode (reflection angle $\alpha = 75^\circ$) with a resolution of 4 cm⁻¹ for an integrated time of
15 2.0 min [5]. After the irradiation, the ices were kept isothermally for 60 min before being heated
16 to 300 K with 0.5 K min⁻¹.
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24 3. Theoretical Methods

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26 The probable isomers of CS_x (x = 3-6) were characterized by *ab initio* electronic structure
27 calculations. Their optimized geometries and harmonic frequencies were obtained at level of
28 MP2 theory with cc-pVTZ basis set [39]; the energies were refined further by CCSD(T) /cc-
29 pVTZ [40, 41] with MP2/cc-pVTZ zero-point energy corrections. The GAUSSIAN09 program
30 was employed in the calculations [42].
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37 4. Theoretical Results

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39 The optimized structures of distinct CS_x (x = 3-6) isomers calculated at the MP2/cc-pVTZ
40 level of theory along with their relative energies obtained at the CCSD(T)/cc-pVTZ level of
41 theory are compiled in Figure 2. The vibrational modes of the CS_x (x = 3-6) isomers as well as
42 their infrared integrated absorption coefficients are also computed and compiled in the
43 Supporting Information. For the carbon trisulfide (CS₃), the geometry optimizations reveal four
44 stable minima on the singlet surface belonging to the C_{2v} (1), C_s (2), D_{3h} (3), and C_s (8) point
45 groups. The hitherto experimentally detected C_{2v} and C_s symmetric CS₃ isomers (1) and (2) [35]
46 have the lowest energies with the C_s symmetric isomer energetically unfavorable by 63 kJmol⁻¹.
47 The computations predict further four triplet structures (4) to (7) which can be formally linked to
48 the singlet isomers (2) [(4) and (5)] and (3) [(6) and (7)].
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Considering the CS₄ molecule, three isomers with C_{2v} (1), D_{2d} (2), and C₁ (5) symmetries in their singlet ground states are located. Isomer (1) presents the lowest energy structure, which is very different from a potential CS₄ structure based on a van-der-Waals complex of CS₂ and S₂ reported earlier [37]. The D_{2d} symmetric CS₄ isomer (2) is 84 kJ mol⁻¹ less stable than the CS₄ (1) structure. The lower stability of the D_{2d} isomer compared to the C_{2v} symmetric structure might be attributed to the enhanced ring strain present in the D_{2d} geometry in spite of an extra CS bond (271 kJ mol⁻¹) present in D_{2d} symmetric CS₄ (2), which is even stronger than the sulfur-sulfur single bond (226 kJ mol⁻¹) present in CS₄ (1). The triplet structures (3) and (4) can be formally derived from (1) and (2) by ring opening via cleavage of the sulfur-sulfur bond. Note that the C_{2v} and D_{2d} symmetric CS₄ isomers are similar to those in the isovalent CO₄ molecules [6].

In case of CS₅, eight minima – six on the singlet and two on the triplet surfaces - are located. The C₂ symmetric structure (1) presents the global minimum with its geometry being similar to the experimentally detected isovalent C₂ symmetric CO₅ molecule [7]. The C_{2v} symmetric isomer (2), which was previously reported to be the global minimum [37], is found to be 61 kJ mol⁻¹ less stable than isomer (1).

Finally, with respect to CS₆, seven singlet isomers are found to be stable. Among them, the C₂ symmetric structure is found to have the lowest energy structure; its chemical bonding is similar to the C_s symmetric isovalent CO₆ molecule detected earlier in our laboratory [8].

5. Experimental Results & Discussion

First, we investigate the formation of new molecules during the irradiation at 12 K. Figure 3 depicts the infrared spectra of the pristine ices at 12 K before and after the irradiation at 100 nA, 1000 nA, and 5000 nA; expanded regions are shown in Figure 4. Table 1 compiles the new absorption features along with their vibrational assignments [26, 43]. Figure 4(A) and 4(B) depict the infrared spectra of the frosts in the 2400-1600 cm⁻¹ and 1400-800 cm⁻¹ regions with only two new absorption features appearing after sixty minutes of irradiation at 100 nA. The new absorptions at 1267 cm⁻¹ is assigned as the ν_1 fundamental band of the well-known carbon monosulfide molecule (CS), which is close to the reported band at 1270 cm⁻¹ recorded in an argon matrix [35]. The band at 1248 cm⁻¹ is assigned to the ν_6 fundamental (CS stretching) of carbon trisulfide (CS₃; C_{2v}), which is in good agreement with the literature value of 1263 cm⁻¹

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4 observed in an argon matrix [35]. Note that no other isomers of carbon trisulfide are detected in
5 this experiment (100 nA). Additional carbon-sulfur clusters with the molecular formulae C_3S_2
6 and C_2S_2 are formed at higher irradiation currents (1000 nA and 5000 nA). The positions of the
7 fundamentals of C_3S_2 at 2068 cm^{-1} (ν_{10}) and 1016 cm^{-1} (ν_8) agree nicely with the reported data at
8 2079 cm^{-1} and 1025 cm^{-1} , respectively [26, 28]. The formation of dicarbon disulfide (C_2S_2) can
9 be confirmed via the detection of its ν_6 band at 1164 cm^{-1} , which matches nicely with the
10 reported band position at 1180 cm^{-1} [26, 28]. Figure 4(E) (5000 nA) exhibits a new absorption
11 band at 1670 cm^{-1} , which can be tentatively assigned as ν_1 vibrational mode of dicarbon
12 monosulfide (C_2S). The band at 1089 cm^{-1} (Figure 6) is assigned to higher order carbon sulfur
13 clusters, C_xS_y , potentially of polymeric nature; this absorption was monitored previously by
14 Cataldo et al. during an early stage of CS_2 and C_3S_2 polymerization experiments at low
15 temperatures of 193 K [44-47]. Note that all assignments are also confirmed via their C-12
16 versus C-13 isotopic shifts (Figure 5; Table 1).
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29 Besides the formation of these well-known carbon sulfur species, additional absorption
30 features emerged in the 1045 to 1074 cm^{-1} region (Figures 4(D), 4(F)). In order to establish the
31 origin of these bands, we also conducted experiments with C-13 isotopically labeled carbon
32 disulfide ($^{13}CS_2$). Figure 5 depicts the infrared spectra of the irradiated $^{12}CS_2$ and $^{13}CS_2$ ices; the
33 assignments are compiled in Tables 1 and 2. On the basis of the isotopic shifts alone, Figures 5
34 and 6 clearly confirm that the absorption features in this region are associated with carbon-
35 bearing species. Here, a deconvolution identifies four distinct bands at 1089 cm^{-1} , 1074 cm^{-1} ,
36 1063 cm^{-1} , and 1045 cm^{-1} . Note that C_xS_y were implicated as the carrier of the 1089 cm^{-1} band.
37 Upon ^{13}C labeling, the triplet at 1074 cm^{-1} , 1063 cm^{-1} , and 1045 cm^{-1} shifts to 1041 cm^{-1} , 1028
38 cm^{-1} , and 1015 cm^{-1} in the irradiated $^{13}CS_2$ ices. These shifts by 30 to 36 cm^{-1} can be linked nice-
39 ly to the substitution of C-12 by C-13 [27, 29].
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50 In order to assign these hitherto unknown absorptions, we compared these data with compu-
51 ted vibrational frequencies of C-12 and C-13 labeled CS_x ($x = 4-6$) species. Here, scaling factors
52 are used to compare the calculated vibrational frequencies with the experimentally observed peak
53 positions. Note that the calculated frequencies are computed within the harmonic approximation,
54 but the actual vibrations are anharmonic. Therefore, these scaling factors account for
55 anharmonicity effects, inadequate description of electron correlation, and the use of finite basis
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sets. The recommended value of the scaling factor depends on the level of theory [48]; Merrick et al. [49] determined these values by comparing experimentally determined vibrational frequencies with the calculated values at multiple levels of theory. A scaling factor of 0.97 is used in the present study at MP2/cc-pVTZ level of theory, which is within the error limit of 0.956 ± 0.020 as recommended by Merrick et al. [49] and by the *Computational Chemistry Comparison and Benchmark Database* (CCCBDB) for the MP2/cc-pVTZ level of theory. Further, it should be mentioned that the calculation of vibrational frequencies does not include interactions with neighboring molecules, which can shift the observed band positions in the solid state; vibrational modes are always computed for unperturbed gas phase molecules. Further, the scaling factors can be different for distinct molecules (light versus heavy atoms) and can also depend on the type of the vibrational modes [50]. Therefore, to validate the use of a scaling factor of 0.97, the experimental and calculated vibrational frequencies of C_{2v} symmetric $^{12}CS_3$ and $^{13}CS_3$ structures (1) (Table 2) are compared. The scaled vibrational frequency of $^{12}CS_3(C_{2v})$ at 1240 cm^{-1} matches the calculated position of 1248 cm^{-1} (ν_6) after being scaled by a factor of 0.97. In the $^{13}CS_2$ system, the ν_6 band of $^{13}CS_3(C_{2v})$ is red shifted to 1200 cm^{-1} , which agrees nicely with our calculated value of 1206 cm^{-1} after scaling with same factor 0.97.

Having established the scaling factor, the scaled, computed frequencies of higher carbon sulfide clusters are now compared with the experimentally observed band positions. Here, the absorption feature at 1045 cm^{-1} is assigned to the ν_9 vibrational mode of the D_{2d} symmetric CS_4 isomer (2). The calculated ν_9 vibrational mode (SCS symmetric stretch and SCS anti symmetric stretch) of the $^{12}CS_4(D_{2d})$ structure are calculated at 1047 cm^{-1} after scaling, which matches nicely with the observed band positions. This absorption presents the strongest band for the $^{12}CS_4(D_{2d})$ isomer. None of the remaining vibrational modes could be observed experimentally due to very low absorption coefficients (Supporting Information). Therefore, the confirmation of our assignment of carbon tetrasulfide molecule requires an agreement with the calculated and observed isotopic shift of the C-13 sample. In the $^{13}CS_2$ experiment, $^{13}CS_4(D_{2d})$ is monitored at 1015 cm^{-1} ; this band correlates well with the scaled value of 1009 cm^{-1} . Hence, the consistent agreement of the peak positions of the ν_9 vibrational mode of $^{12}CS_4(D_{2d})$ and $^{13}CS_4(D_{2d})$ with the theoretically predicted shifts confirms our assignment of the D_{2d} symmetric carbon tetrasulfide molecule. It is important to note that, the C_{2v} symmetric isomer (1) is energetically more stable than the experimentally detected D_{2d} symmetric isomer by 84 kJ mol^{-1} . The most intense

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4 vibrational mode of CS₄ (C_{2v}) is calculated at 1141 cm⁻¹ after scaling. However, no absorption
5 could be identified in this region.
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9 Further, the absorption feature at 1074 cm⁻¹ is attributed to the ν_{12} vibrational mode of the C₂
10 symmetric carbon pentasulfide isomer CS₅ (1). After scaling, the calculated ν_{12} vibrational mode
11 (CS stretching) of this isomer is 1080 cm⁻¹ in good agreement with the observed band. In the
12 irradiated ¹³CS₂ ices, the experimental band is shifted to 1041 cm⁻¹; this value matches nicely the
13 computed, scaled ν_{12} vibrational band (CS stretching) at 1046 cm⁻¹. Therefore, on the basis of a
14 consistent agreement of the isotopic shifts of the ν_{12} vibrational modes, the C₂ symmetric carbon
15 pentasulfide isomer CS₅ (1) can be identified. Note that the assigned structure presents the
16 thermodynamically most stable isomer among the calculated structures of carbon pentasulfide.
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24 Finally, the absorption band at 1063 cm⁻¹ suggests the formation of a CS₆ isomer. Here, the
25 ν_{15} fundamental band (CS stretching) of the C₂ symmetric carbon hexasulfide isomer CS₆ (1)
26 calculates after scaling to be 1079 cm⁻¹ close to the experimental data. The isotopic shift is
27 determined experimentally and theoretically, too. The detection the ν_{15} band of ¹³CS₆ (C₂) at
28 1028 cm⁻¹ in the ¹³CS₂ experiment is in close agreement with the calculated band at 1046 cm⁻¹
29 after scaling. Note that using recommended scaling factor of 0.956 for MP2/cc-pVDZ level, the
30 calculated ν_{15} vibrational mode of ¹²CS₆ and ¹³CS₆ are calculated to be 1063 cm⁻¹ and 1031 cm⁻¹,
31 respectively, which are even closer to the experimentally observed bands at 1063 cm⁻¹ and 1028
32 cm⁻¹. Therefore, based on the calculated and observed isotopic shifts, we suggest the detection of
33 the most stable, C₂ symmetric CS₆ isomer. Finally, the ratio of the observed and calculated
34 harmonic vibrational frequencies of the CS_x (x = 3-5) species and their isotopologues are also
35 calculated (Table 2). The average value of these ratios is calculated to be 0.971 ± 0.005, which is
36 within the limit of recommended scaling factor of 0.956 ± 0.020 and close to our chosen scaling
37 factor of 0.97.
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51 In order to account for the stability of the assigned CS_x (x = 4-6) species, we also
52 monitored the fate of the observed bands (1074 cm⁻¹ to 1045 cm⁻¹) during warm up phase to 300
53 K. For comparison, neat carbon disulfide sublimates at about 130 K. The absorption band at 1045
54 cm⁻¹ (CS₄; D_{2d}) was observed to be stable up to temperature of 75 K, when it declined sharply,
55 where as the other two bands at 1074 cm⁻¹ (CS₅; C₂), and 1063 cm⁻¹ (CS₆; C₂) only decreased
56 with the sublimation of the carbon disulfide matrix at 130 K. This clearly indicates the instability
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of carbon tetrasulfide (CS_4 ; D_{2d}) at temperatures above 75 K. Finally, we would like to discuss the possibility of other molecules, which contain carbon-sulfur functional groups, contributing to the region of 1074 cm^{-1} to 1045 cm^{-1} . Vala et al. investigated the infrared absorptions of a series of C_nS ($n = 1-7$) and C_mS_2 ($m = 1-15$) [27, 28] species. A comparison of their data with the newly emerging peaks in our experiments clearly indicates that none of the C_nS and C_mS_2 molecules holds any vibrational absorption features in 1100 cm^{-1} to 1000 cm^{-1} spectral region, except the ν_8 band of the C_3S_2 species at 1016 cm^{-1} , which is already assigned. Further, except the assigned CS , C_2S , C_2S_2 , and C_3S_2 molecules, there is no evidence of the formation of any other C_nS and C_nS_2 species in the present experiment.

6. Summary

We have detected the carbon trisulfide (CS_3 ; C_{2v}) and for the very first time carbon tetrasulfide (CS_4 ; D_{2d}), carbon pentasulfide (CS_5 ; C_2), and carbon hexasulfide (CS_6 , C_2) molecules in low temperature carbon disulfide ices. The stabilities of the molecules are verified by ab initio calculations. The infrared spectroscopic study along with experimental and calculated isotopic shifts of the ν_{12} vibrational band of carbon tetrasulfide confirms the detection of the higher energy D_{2d} symmetric isomer. The detection of CS_5 (C_2) and CS_6 (C_2) molecules is supported by an excellent agreement of the observed peak positions of C-12 and C-13 isotopologues with our ab initio calculations (Table 2). The CS_x ($x=3-6$) molecules - similar to CO_x ($x=3-6$) - may be useful as prototype molecules to study high energy materials, which can store large amount of energy of up to $1,000\text{ kJ mol}^{-1}$. Since the experiments were not conducted under gas phase single collision conditions, it has been proven difficult to elucidate detailed formation mechanisms of the newly synthesized CS_x ($x=3-6$) molecules. However, an analysis of the temporal evolution of the absorption features indicates that CS_x ($x=3-6$) molecules might be synthesized via rapid additions of sulfur atoms and/or small sulfur clusters such as disulfur from their simple precursors.

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Supporting Information

Possible formation pathways (Scheme S1) of the newly formed molecules are discussed in this section. The evolution of column densities during the irradiation at 100 nA, 1000 nA, and 5000 nA along with the kinetic fits (Figure S1 and Figure S2) and rate constants (Table S1) are also available. The energies of CS_x ($x=3-6$) together with the vibrational modes are also available (Table S2 and Table S3). The infrared spectra of the residues are also given at 300 K (Figure S3).

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Table 1: Infrared absorption features recorded before and after the irradiation of C-12 and C-13 carbon disulfide (CS₂) ices at 12 K

Irradiation		Literature Assignment			
Before (cm ⁻¹)	After (cm ⁻¹)	Ref.	(cm ⁻¹)	Assignment	Carrier
2283	...	[26, 43]	2324	2ν ₂ + ν ₃	CS ₂
2210	...	[26, 43]	2249	2ν ₂ + ν ₃	¹³ CS ₂
2158	...	[26, 43]	2178	ν ₁ + ν ₃	CS ₂
2096	...	[26, 43]	2128	ν ₁ + ν ₃	¹³ CS ₂
...	2068	[26, 28]	2079	ν ₁₀	C ₃ S ₂
...	1981	[26, 28]	1998	ν ₁₀	¹³ C ₃ S ₂
...	1670	[27]	1664	ν ₁	C ₂ S
...	1611	ν ₁	¹³ C ₂ S
1524	...	[26, 43]	1528	ν ₃	CS ₂
1461	...	[26, 43]	1475	ν ₃	¹³ CS ₂
...	1267	[35]	1270	ν ₁	CS
...	1233	[26, 28]	1240	ν ₁	¹³ CS
...	1248	[35]	1263	ν ₆	CS ₃
...	1206	[35]	1219	ν ₆	¹³ CS ₃
...	1164	[26, 28]	1180	ν ₆	C ₂ S ₂
...	1136	[26, 28]	1146	ν ₆	¹³ C ₂ S ₂
...	1089	[47]	1073	ν _{cs}	C _x S _y
...	1052	ν _{cs}	¹³ C _x S _y
...	1074-1038	ν _{cs}	CS _{x(x=4-6)}
...	1041-1015	ν _{cs}	¹³ CS _{x(x=4-6)}
...	1016	[26, 28]	1025	ν ₈	C ₃ S ₂
...	992	[26, 28]	998	ν ₈	¹³ C ₃ S ₂

Table 2: The observed positions of the CS₃, CS₄, CS₅, and CS₆ molecules together with their C-13 counterparts compared to the scaled computed frequencies calculated at the MP2/ cc-pVTZ level of theory.

Species	Vibrational mode	Observed Frequency (cm ⁻¹)	Calculated Frequency (cm ⁻¹)	Scaled Frequency (cm ⁻¹)	Ratio of observed and calculated frequency	Scaling Factor
¹² CS ₃ (C _{2v})	v ₆	1248	1279	1240	0.975	0.970
¹³ CS ₃ (C _{2v})	v ₆	1206	1238	1200	0.974	0.970
¹² CS ₄ (D _{2d})	v ₉	1045	1079	1047	0.968	0.970
¹³ CS ₄ (D _{2d})	v ₉	1015	1040	1009	0.976	0.970
¹² CS ₅ (C ₂)	v ₁₂	1074	1113	1080	0.965	0.970
¹³ CS ₅ (C ₂)	v ₁₂	1041	1078	1046	0.966	0.970
¹² CS ₆ (C ₂)	v ₁₅	1063	1112	1079 (1063)	0.955	0.970 (0.956)
¹³ CS ₆ (C ₂)	v ₁₅	1028	1078	1046 (1031)	0.954	0.970 (0.956)

Figure Captions

Figure 1. Structures of detected CO_3 (C_{2v} and D_{3h}), CO_4 (C_{2v} and D_{2d}), CO_5 (C_2) and CO_6 (C_s) species. The $\text{CO}_4(\text{D}_{2d})$ isomer was assigned tentatively.

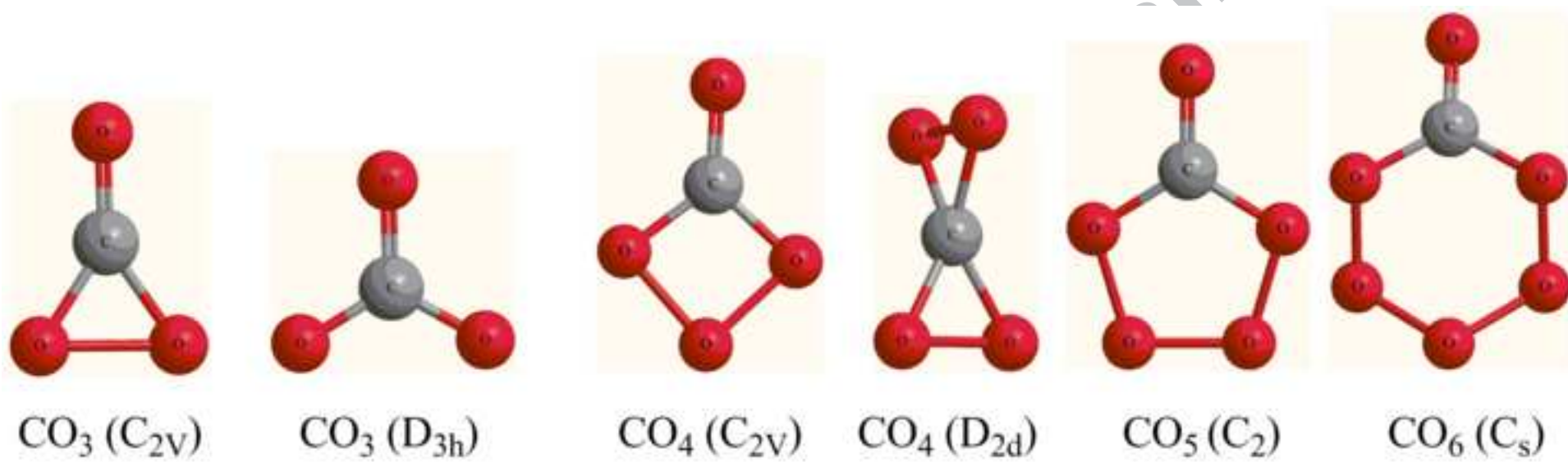
Figure 2: Geometry optimized structures of CS_x ($x=3-6$). The geometry optimizations and zero point energy corrections were conducted at the MP2/cc-pVTZ level of theory. Relative energies (shown in bracket in kJ mol^{-1}) were calculated after single point calculations of optimized structures at CCSD(T)/cc-pVTZ level with zero point energy corrections using the MP2/cc-pVTZ level. Bond lengths (in angstrom) and bond angles (in degree) are also shown.

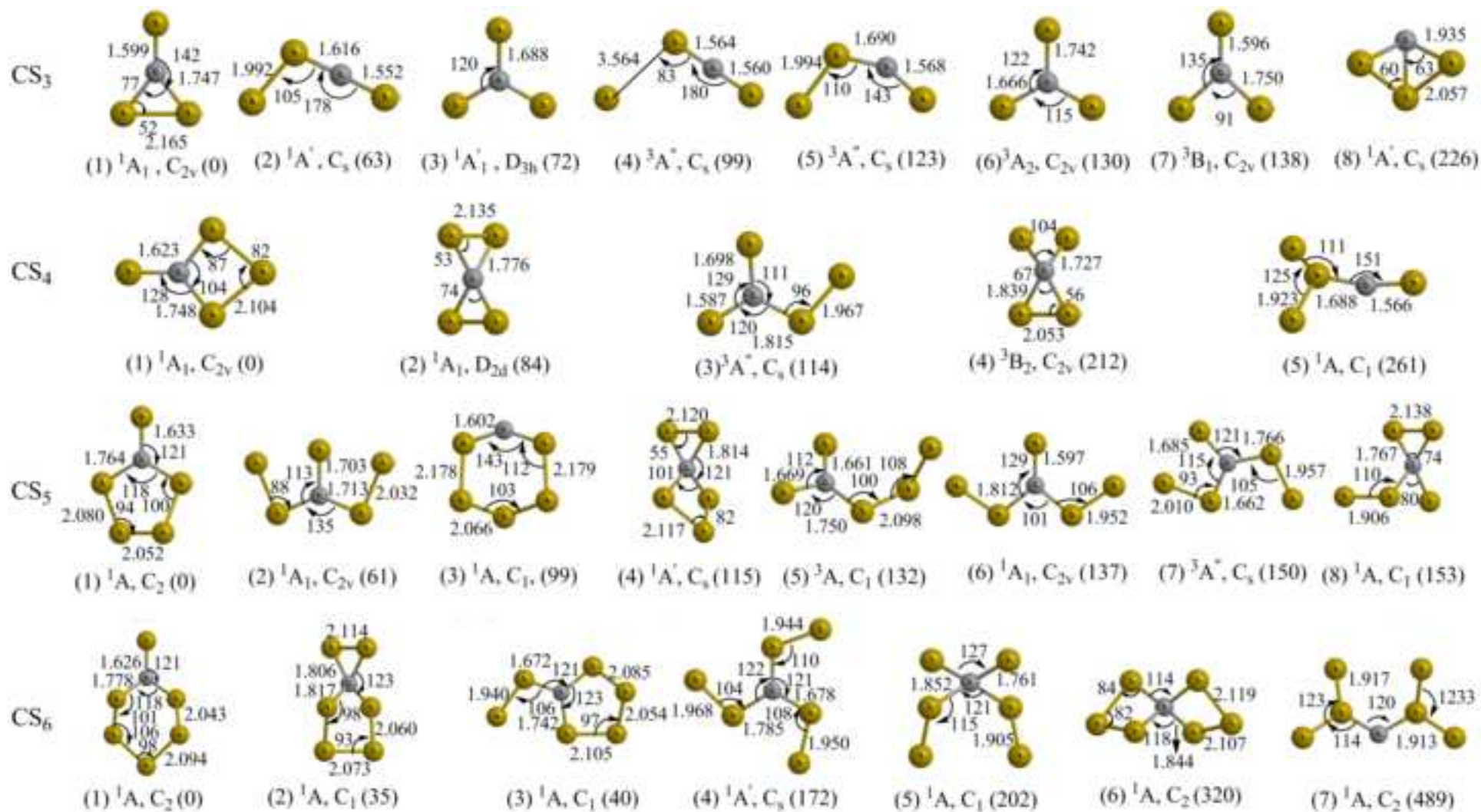
Figure 3: Infrared spectra of carbon disulfide (CS_2) ices before the irradiation (dashed trace) and after the irradiation (solid trace) at three different irradiation currents: (A) 100 nA (1 hour), (B) 1000 nA (3 hours) and (C) 5000 nA (3 hours) at 12 K.

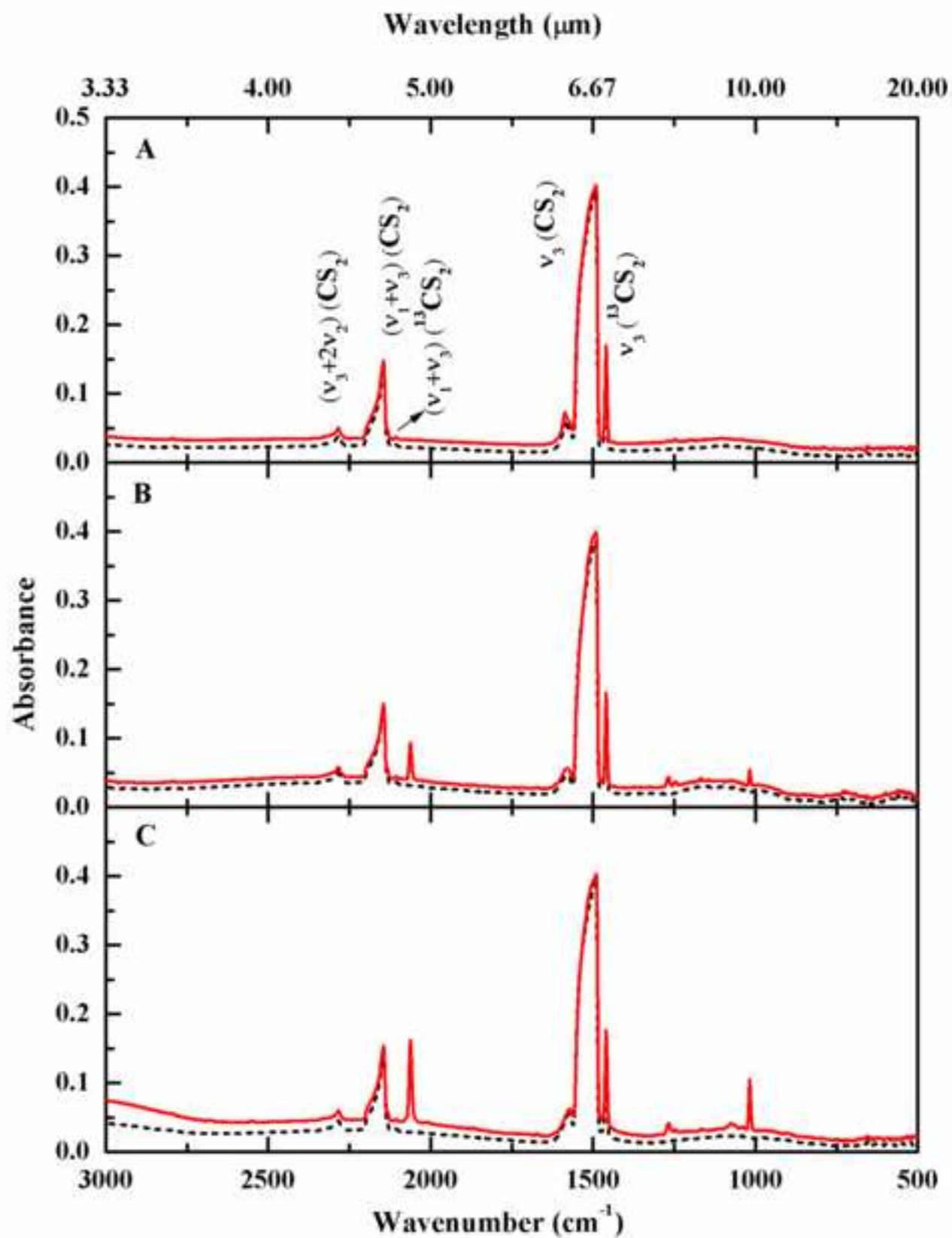
Figure 4: Infrared spectra of the species formed during the irradiation of carbon disulfide (CS_2) ices at three different currents: (A, B) 100 nA (1 hour), (C, D) 1000 nA (3 hours) and (E, F) 5000 nA (3 hours) at 12 K. Dashed traces indicate spectra before the irradiation and the solid traces after the irradiation.

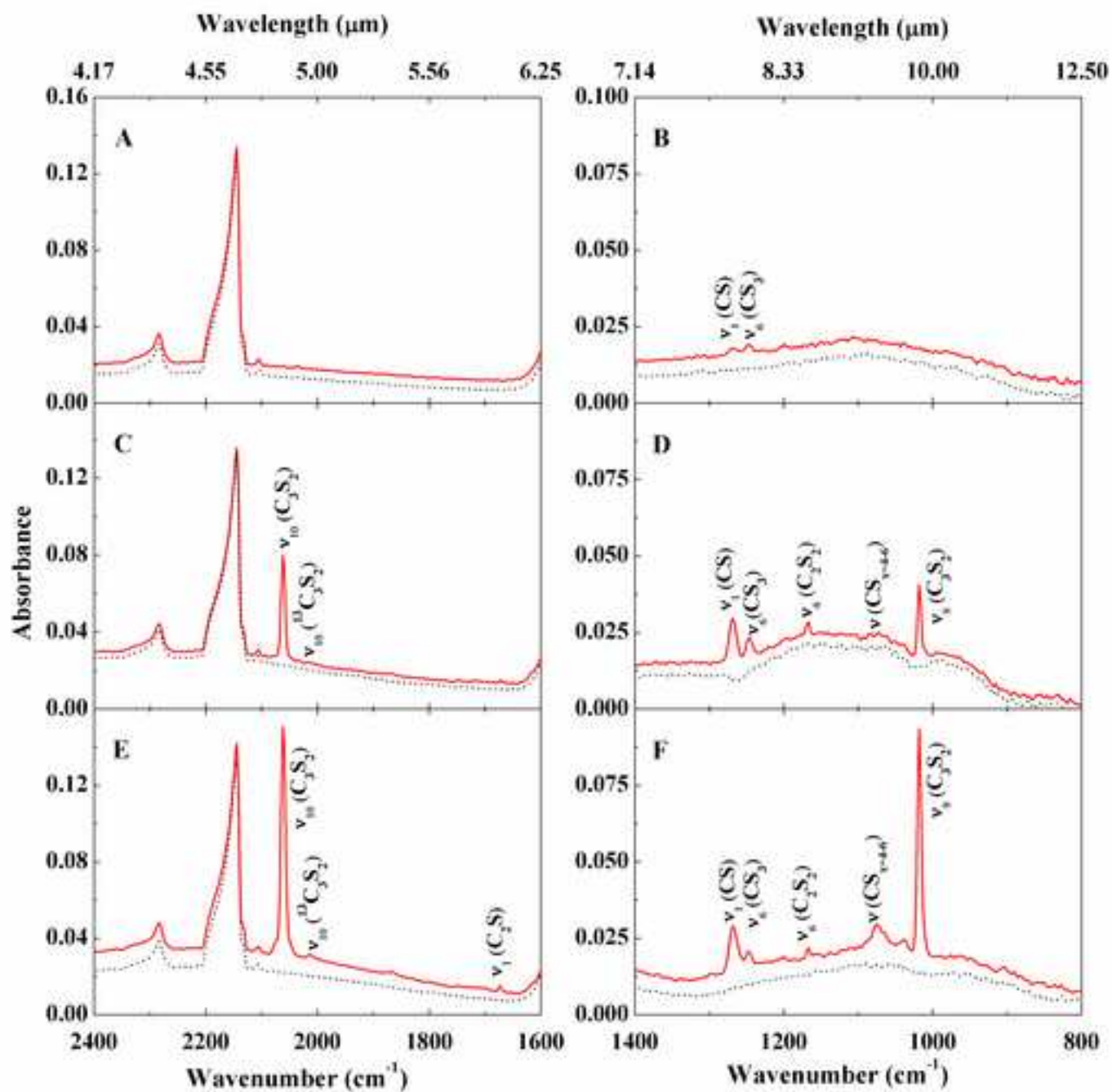
Figure 5: Infrared Spectra of irradiated $^{12}\text{CS}_2$ (bottom panel) and $^{13}\text{CS}_2$ (top panel) ices (5000 nA).

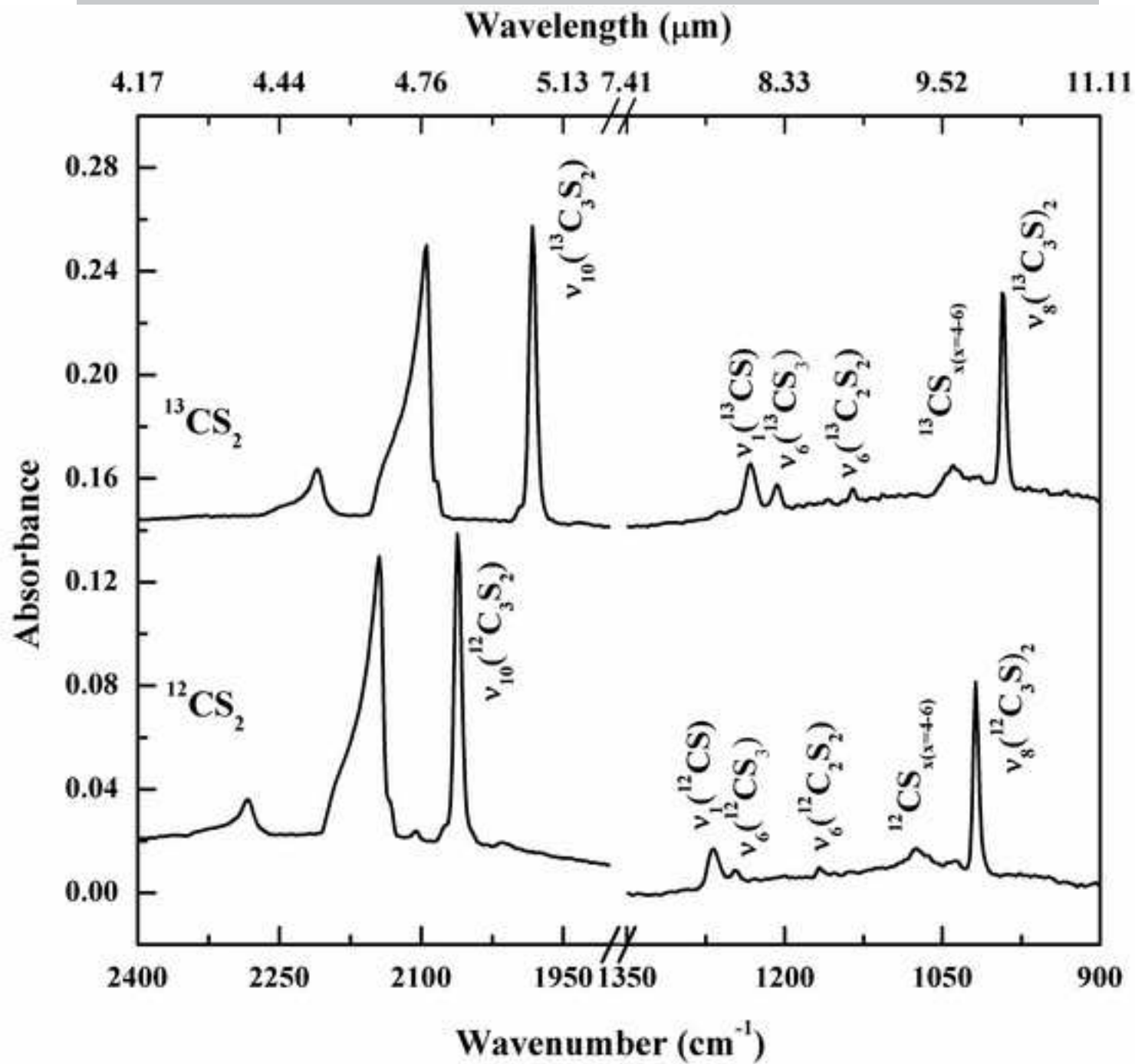
Figure 6: Peak deconvolution of the 1000 to 1130 cm^{-1} region of irradiated $^{12}\text{CS}_2$ (bottom) and $^{13}\text{CS}_2$ (top) ices (5000 nA).

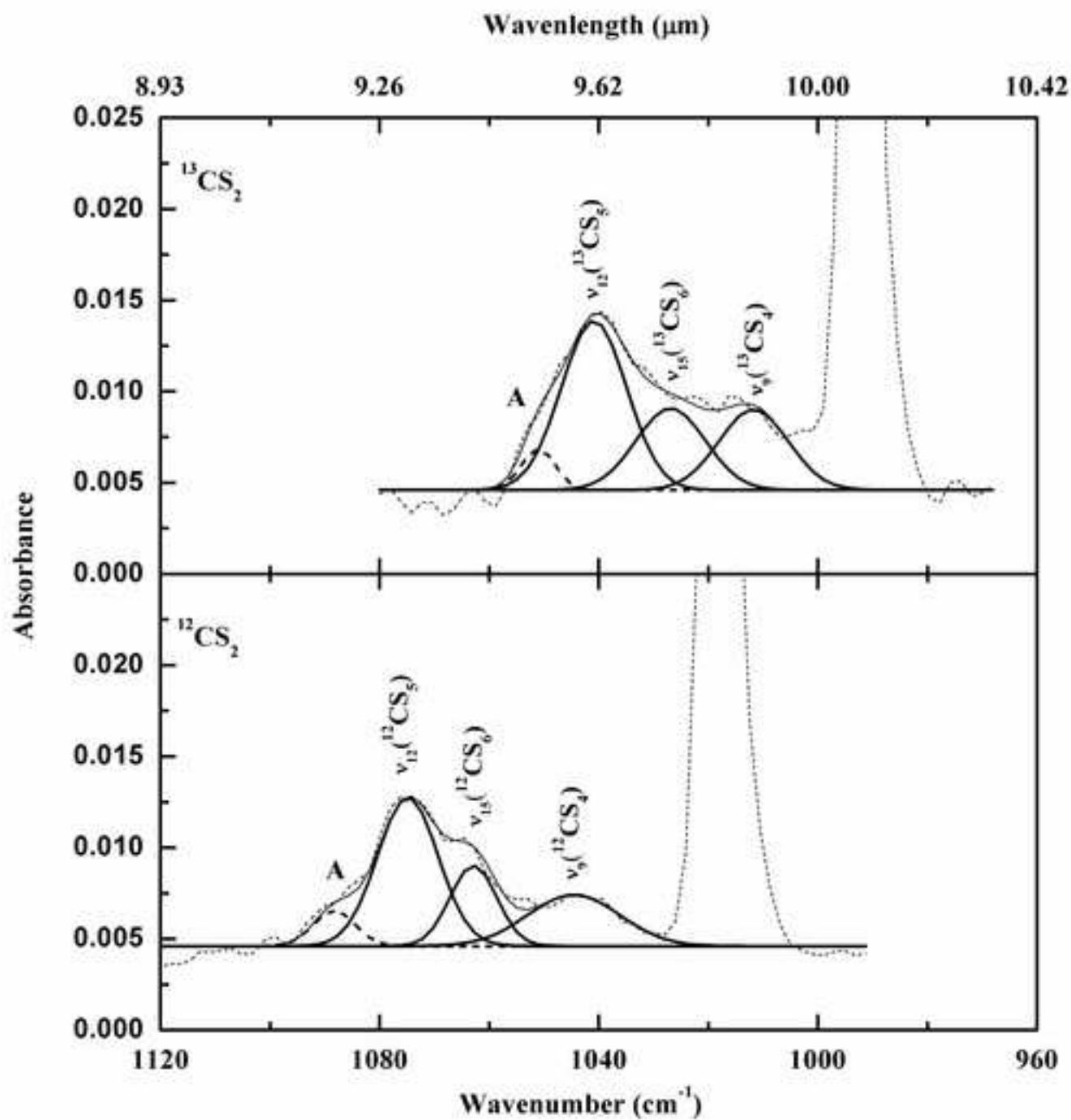






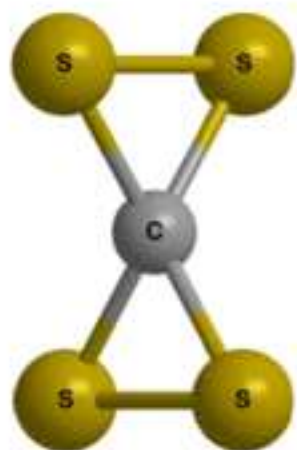
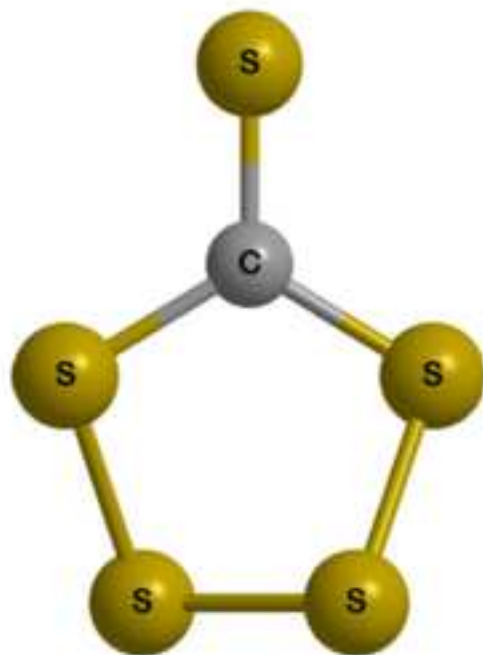
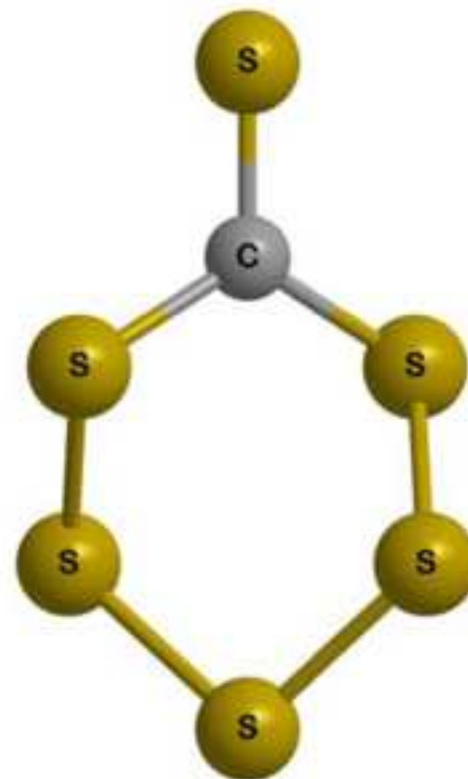






- Higher carbon sulfides CS_x ($x=4-6$) are detected in electron irradiated CS_2 ices
- The products are monitored via infrared spectroscopic detection at 12K
- *ab initio* calculations are used to predict the structures and IR frequencies
- Observed and calculated isotopic shifts are used to verify the assignments
- The stabilities of the products are verified at higher temperatures

ACCEPTED MANUSCRIPT

 CS_4  CS_5  CS_6