



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

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ABSTRACT

Higher-order carbon sulfides – carbon tetrasulfide (CS_4 ; D_{2q}), 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.

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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 ($x = 3\text{--}6$) 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. 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 interest 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 ($n = 1\text{--}3$, $m = 1\text{--}2$) have attracted attention from the planetary science community, when fragments of comet Shoemaker-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 molecules as well [26]. A series of small carbon sulfur clusters (C_nS ($n = 1\text{--}7$) and C_mS_2 ($m = 1\text{--}15$)) 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 the presence of an inert gas bath [31]. Engelke et al. as well as Sulzle et al. confirmed the formation of carbon trisulfide via mass spectroscopy [32,33]. Fueled by these experiments, Froese et al. conducted electronic structure calculations and suggested that three isomers may exist: carbon trisulfide in C_{2v} and D_{3h} geometries as well as a bent, C_s -symmetric SCSS isomer [34]. A recent infrared spectroscopic study by Ma et al. identified the C_{2v} and C_s -symmetric carbon trisulfide isomers in an argon matrix; high level *ab initio* calculations revealed that C_{2v} -symmetric carbon trisulfide isomer presents the global energy minimum [35,36]. Here, the molecular structure of the cyclic C_{2v} symmetric carbon trisulfide is similar to the isovalent C_{2v} structure of the cyclic carbon trioxide (CO_3) molecule [5]. Note that the D_{3h} symmetric CO_3 isomer was also identified, whereas the isovalent CS_3 isomer was not confirmed experimentally [5,35]. The molecular structures of CS_4 and CS_5 were investigated computationally using B3LYP/6-311G* level of theory [37]. The study revealed that the structure of CS_4 can be characterized as a van-der-Waals complex of CS_2 with S_2 , in which the sulfur–sulfur distance between CS_2 and S_2 moiety was 4.358 Å. The molecular structure of CS_4 was distinctly different

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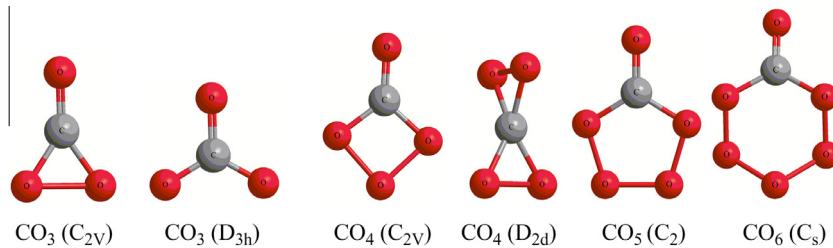


Figure 1. Structures of detected CO_3 ($\text{C}_{2\text{v}}$ and $\text{D}_{3\text{h}}$), CO_4 ($\text{C}_{2\text{v}}$ and $\text{D}_{2\text{d}}$), CO_5 (C_2) and CO_6 (Cs) species. The CO_4 ($\text{D}_{2\text{d}}$) isomer was assigned tentatively.

from its isovalent carbon tetraoxide (CO_4 ; $\text{C}_{2\text{v}}$) molecule (Figure 1) [6]. Similarly, the structure reported for of CS_5 ($\text{C}_{2\text{v}}$) was characterized by $\text{S}_2\text{C}(\text{S})\text{S}_2$ which was distinctly different from the carbon pentaoxide (CO_5) (C_2) structure [7]. Note that the existence of sulfur chains (S_n) were reported in the single crystal structure of carbon–sulfur clusters C_3S_8 and C_6S_{12} [38].

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

2. Experimental methods

The experiments were carried out in a contamination-free ultra high vacuum (UHV) chamber at a base pressure 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 ($^{12}\text{CS}_2$, Acros Organics, 99.9%; $^{13}\text{CS}_2$, Cambridge Isotope Lab, 97–99 atom ^{13}C %) was introduced into the main chamber at a pressure of 1.2×10^{-7} Torr via a

precision leak valve and a glass capillary array and condensed on the cooled substrate for 10 min. This resulted carbon disulfide ice films with thicknesses of 300 ± 8 nm [5].

The ice sample was then irradiated isothermally at 12 K with 5 keV electrons generated by an electron gun (SPECS; EQ 22/35) at a nominal beam current of 0 (blank) 100, 1000, and 5000 nA over an area of 3.0 ± 0.2 cm 2 . The radiation-induced chemical reactions in the ices were monitored on line and in situ by a Nicolet Infrared Spectrometer (Nicolet 6700) in a spectral range of 6000–500 cm $^{-1}$. Each FTIR spectrum was recorded in absorption–reflection–absorption mode (reflection angle $\alpha = 75^\circ$) with a resolution of 4 cm $^{-1}$ for an integrated time of 2.0 min [5]. After the irradiation, the ices were kept isothermally for 60 min before being heated to 300 K with 0.5 K min $^{-1}$.

3. Theoretical methods

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

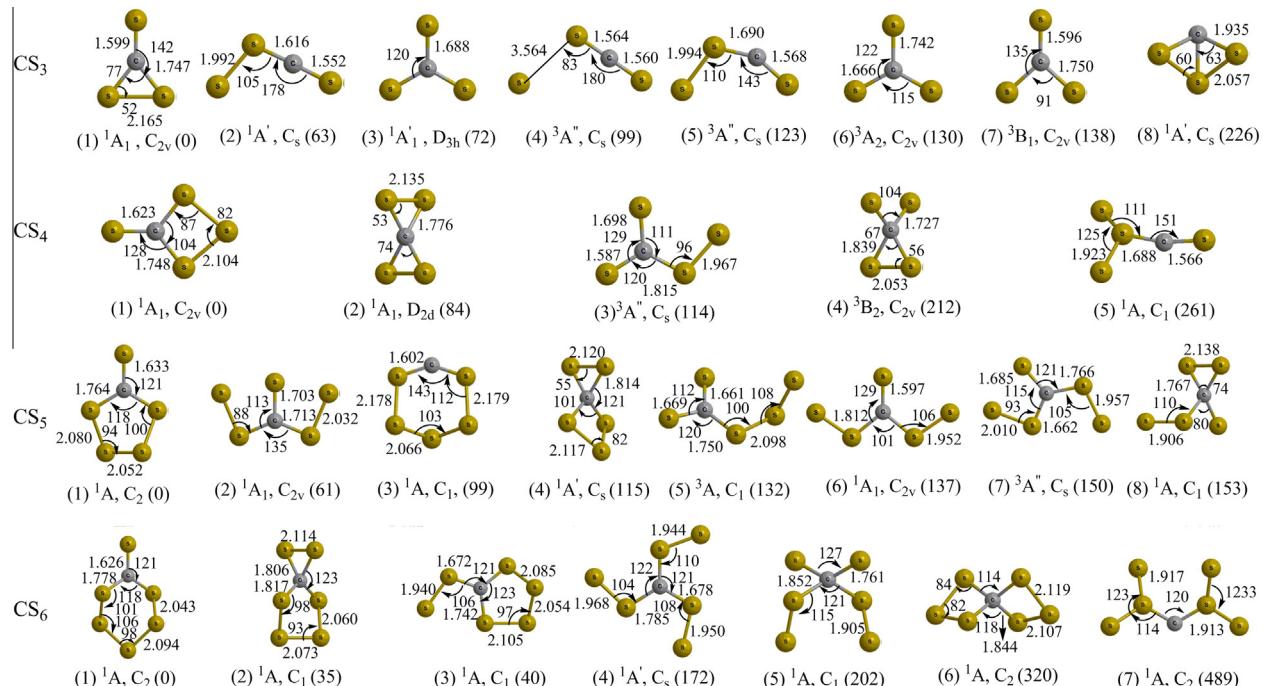


Figure 2. Geometry optimized structures of CS_x ($x = 3\text{--}6$). The geometry optimizations and zero point energy corrections were conducted at the MP2/cc-pVTZ level of theory. Relative energies (shown in bracket in kJ mol $^{-1}$) were calculated after single point calculations of optimized structures 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.

4. Theoretical results

The optimized structures of distinct CS_x ($x = 3\text{--}6$) isomers calculated at the MP2/cc-pVTZ level of theory along with their relative energies obtained at the CCSD(T)/cc-pVTZ level of theory are compiled in Figure 2. The vibrational modes of the CS_x ($x = 3\text{--}6$) isomers as well as their infrared integrated absorption coefficients are also computed and compiled in the Supporting Information. For the carbon trisulfide (CS_3), the geometry optimizations reveal four stable minima on the singlet surface belonging to the C_{2v} (1), C_s (2), D_{3h} (3), and C_s (8) point groups. The hitherto experimentally detected C_{2v} and C_s symmetric CS_3 isomers (1) and (2) [35] have the lowest energies with the C_s symmetric isomer energetically unfavorable by 63 kJ mol⁻¹. The computations predict further four triplet structures (4) to (7) which can be formally linked to the singlet isomers (2) [(4) and (5)] and (3) [(6) and (7)].

Considering the CS_4 molecule, three isomers with C_{2v} (1), D_{2d} (2), and C_1 (5) symmetries in their singlet ground states are located. Isomer (1) presents the lowest energy structure, which is very different from a potential CS_4 structure based on a van-der-Waals complex of CS_2 and S_2 reported earlier [37]. The D_{2d} symmetric CS_4 isomer (2) is 84 kJ mol⁻¹ less stable than the CS_4 (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 CS_4 (2), which is even stronger than the sulfur-sulfur single bond (226 kJ mol⁻¹) present in CS_4 (1). The triplet structures (3) and (4) can be formally derived from (1) and (2), respectively, by ring opening via cleavage of the sulfur-sulfur bond. Note that the C_{2v} and D_{2d} symmetric CS_4 isomers are similar to those in the isovalent CO_4 molecules [6].

In case of CS_5 , eight minima – six on the singlet and two on the triplet surfaces – are located. The C_2 symmetric structure (1) presents the global minimum with its geometry being similar to the experimentally detected isovalent C_2 symmetric CO_5 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 CS_6 , seven singlet isomers are found to be stable. Among them, the C_2 symmetric structure is found to have the lowest energy structure; its chemical bonding is similar to the C_s symmetric isovalent CO_6 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, 1000, 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 4A and B depict the infrared spectra of the frosts in the 2400–1600 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 v_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 v_6 fundamental (CS stretching) of carbon trisulfide (CS_3 ; C_{2v}), which is in good agreement with the literature value of 1263 cm⁻¹ observed in an argon matrix [35]. Note that no other isomers of carbon trisulfide are detected in this experiment (100 nA). Additional carbon–sulfur clusters with the molecular formulae C_3S_2 and C_2S_2 are formed at higher irradiation currents (1000 and 5000 nA). The positions of the fundamentals of C_3S_2 at 2068 cm⁻¹

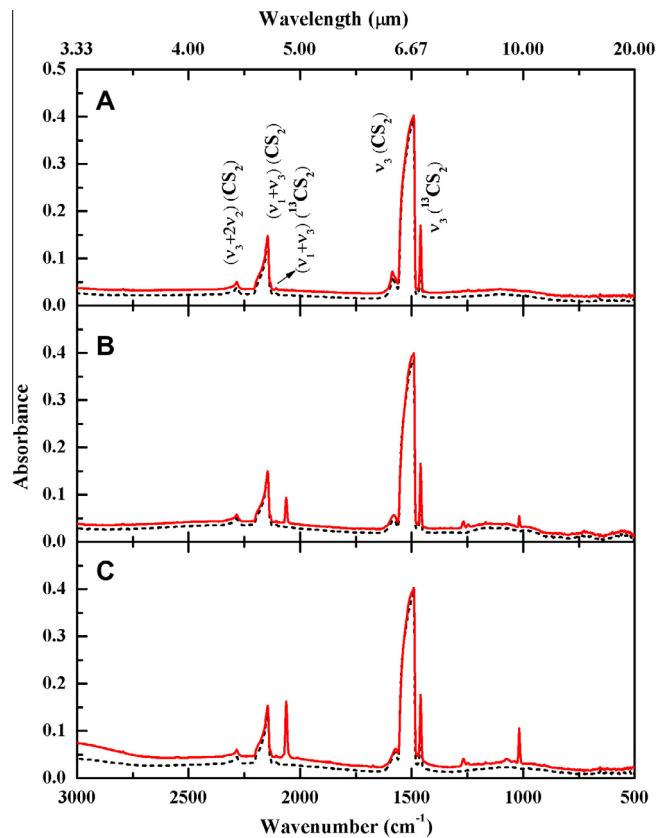


Figure 3. Infrared spectra of carbon disulfide (CS_2) ices before the irradiation (dashed trace) and after the irradiation (solid trace) at three different irradiation currents: (A) 100 nA (1 h), (B) 1000 nA (3 h) and (C) 5000 nA (3 h) at 12 K.

(v_{10}) and 1016 cm⁻¹ (v_8) agree nicely with the reported data at 2079 and 1025 cm⁻¹, respectively [26,28]. The formation of dicarbon disulfide (C_2S_2) can be confirmed via the detection of its v_6 band at 1164 cm⁻¹, which matches nicely with the reported band position at 1180 cm⁻¹ [26,28]. Figure 4E (5000 nA) exhibits a new absorption band at 1670 cm⁻¹, which can be tentatively assigned as the v_1 vibrational mode of dicarbon monosulfide (C_2S). The band at 1089 cm⁻¹ (Figure 6) is assigned to higher order carbon sulfur clusters, C_xS_y , potentially of polymeric nature; this absorption was monitored previously by Cataldo et al. during an early stage of CS_2 and C_3S_2 polymerization experiments at low temperature of 193 K [44–47]. Note that all assignments are also confirmed via their C-12 versus C-13 isotopic shifts (Figure 5; Table 1).

Besides the formation of these well-known carbon sulfur species, additional absorption features emerged in the 1045 to 1074 cm⁻¹ region (Figures 4D and F). In order to establish the origin of these bands, we also conducted experiments with C-13 isotopically labeled carbon disulfide ($^{13}\text{CS}_2$). Figure 5 depicts the infrared spectra of the irradiated $^{12}\text{CS}_2$ and $^{13}\text{CS}_2$ ices; the assignments are compiled in Tables 1 and 2. On the basis of the isotopic shifts alone, Figures 5 and 6 clearly confirm that the absorption features in this region are associated with carbon-bearing species. Here, a deconvolution identifies four distinct bands at 1089, 1074, 1063, and 1045 cm⁻¹. Note that C_xS_y were implicated as the carrier of the 1089 cm⁻¹ band. Upon ^{13}C labeling, the triplet at 1074, 1063, and 1045 cm⁻¹ shifts to 1041, 1028, and 1015 cm⁻¹ in the irradiated $^{13}\text{CS}_2$ ices. These shifts by 30–36 cm⁻¹ can be linked nicely to the substitution of C-12 by C-13 [27,29].

In order to assign these hitherto unknown absorptions, we compared these data with computed vibrational frequencies of C-12

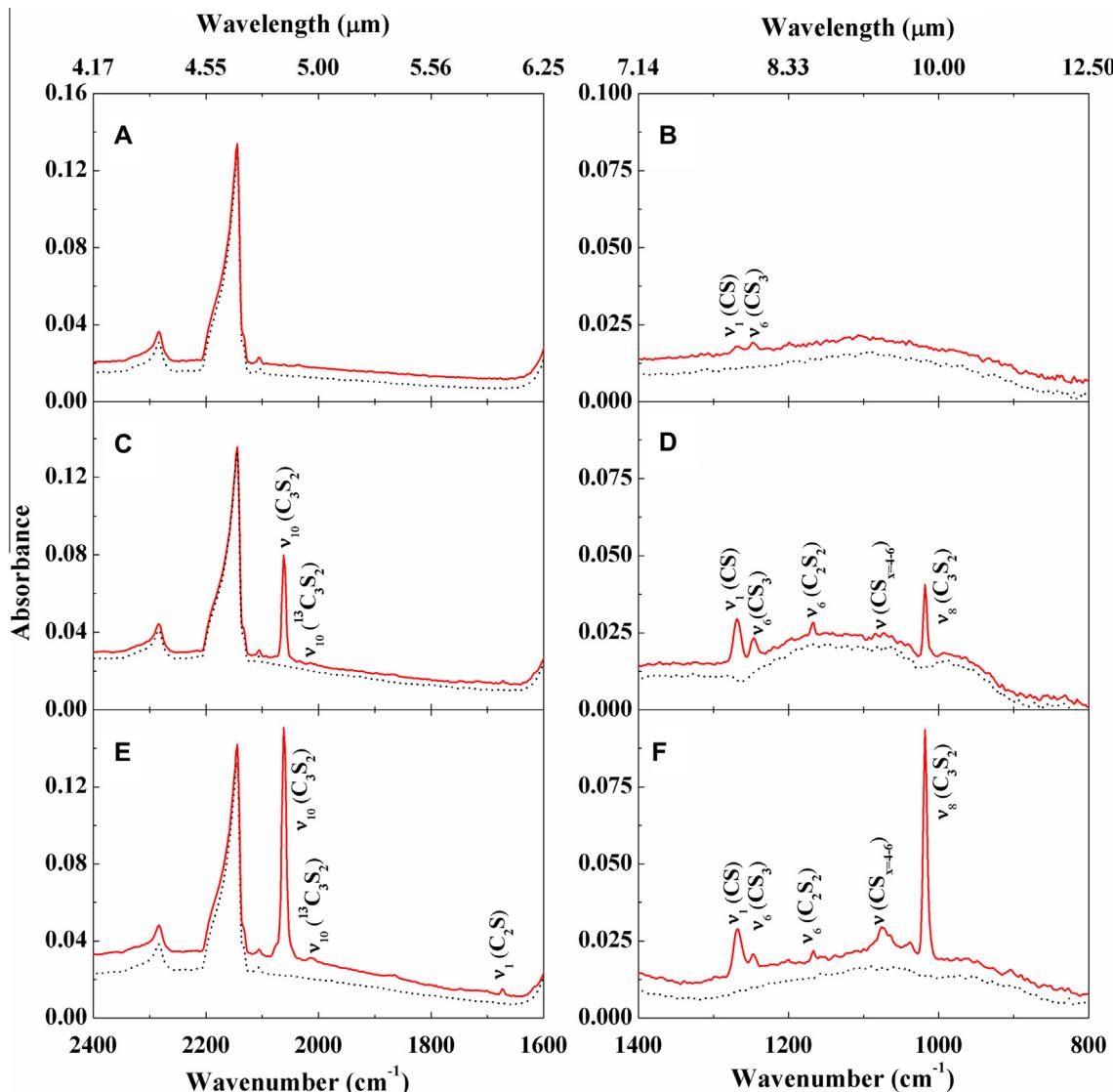


Figure 4. Infrared spectra of the species formed during the irradiation of carbon disulfide (CS_2) ices at three different currents: (A, B) 100 nA (1 h), (C, D) 1000 nA (3 h) and (E, F) 5000 nA (3 h) at 12 K. Dashed traces indicate spectra before the irradiation and the solid traces after the irradiation.

and C-13 labeled CS_x ($x = 4-6$) species. Here, scaling factors are used to compare the calculated vibrational frequencies with the experimentally observed peak positions. Note that the calculated frequencies are computed within the harmonic approximation, but the actual vibrations are anharmonic. Therefore, these scaling factors account for anharmonicity effects, inadequate description of electron correlation, and the use of finite basis 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 vali-

date the use of a scaling factor of 0.97, the experimental and calculated vibrational frequencies of C_{2v} symmetric $^{12}\text{CS}_3$ and $^{13}\text{CS}_3$ structures (1) (Table 2) are compared. The scaled vibrational frequency of $^{12}\text{CS}_3(\text{C}_{2v})$ at 1240 cm^{-1} matches with the calculated position of 1248 cm^{-1} (ν_6) after being scaled by a factor of 0.97. In the $^{13}\text{CS}_2$ system, the ν_6 band of $^{13}\text{CS}_3(\text{C}_{2v})$ is red shifted to 1200 cm^{-1} , which agrees nicely with our calculated value of 1206 cm^{-1} after scaling with the same factor of 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 $^{12}\text{CS}_4$ (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 $^{12}\text{CS}_4$ (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 $^{13}\text{CS}_2$

Table 1

Infrared absorption features recorded before and after the irradiation of C-12 and C-13 carbon disulfide (CS_2) ices at 12 K.

Irradiation		Literature assignment		
Before (cm^{-1})	After (cm^{-1})	Ref.	(cm^{-1})	Assignment
2283	...	[26,43]	2324	$2\nu_2 + \nu_3$
2210	...	[26,43]	2249	$2\nu_2 + \nu_3$
2158	...	[26,43]	2178	$\nu_1 + \nu_3$
2096	...	[26,43]	2128	$\nu_1 + \nu_3$
...	2068	[26,28]	2079	ν_{10}
...	1981	[26,28]	1998	ν_{10}
...	1670	[27]	1664	ν_1
...	1611	ν_1
1524	...	[26,43]	1528	ν_3
1461	...	[26,43]	1475	ν_3
...	1267	[35]	1270	ν_1
...	1233	[26,28]	1240	ν_1
...	1248	[35]	1263	ν_6
...	1206	[35]	1219	ν_6
...	1164	[26,28]	1180	ν_6
...	1136	[26,28]	1146	ν_6
...	1089	[47]	1073	ν_{cs}
...	1052	ν_{cs}
...	1074–1038	ν_{cs}
...	1041–1015	ν_{cs}
...	1016	[26,28]	1025	ν_8
...	992	[26,28]	998	ν_8
				$^{13}\text{C}_3\text{S}_2$

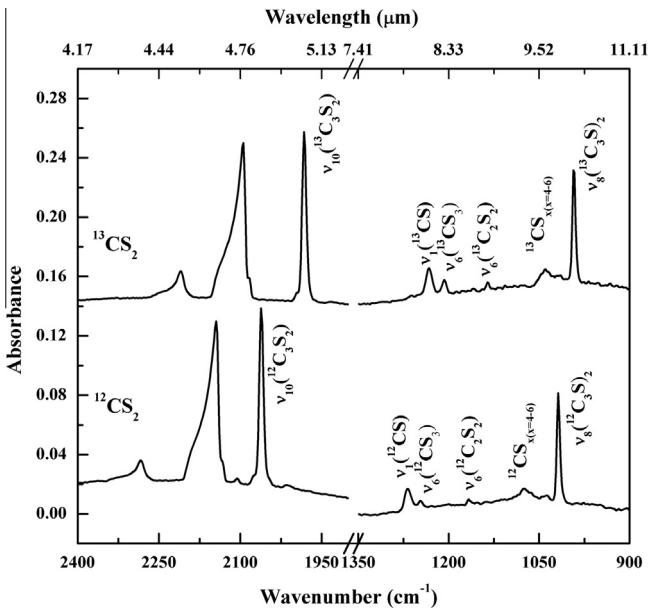


Figure 5. Infrared Spectra of irradiated $^{12}\text{CS}_2$ (bottom panel) and $^{13}\text{CS}_2$ (top panel) ices (5000 nA).

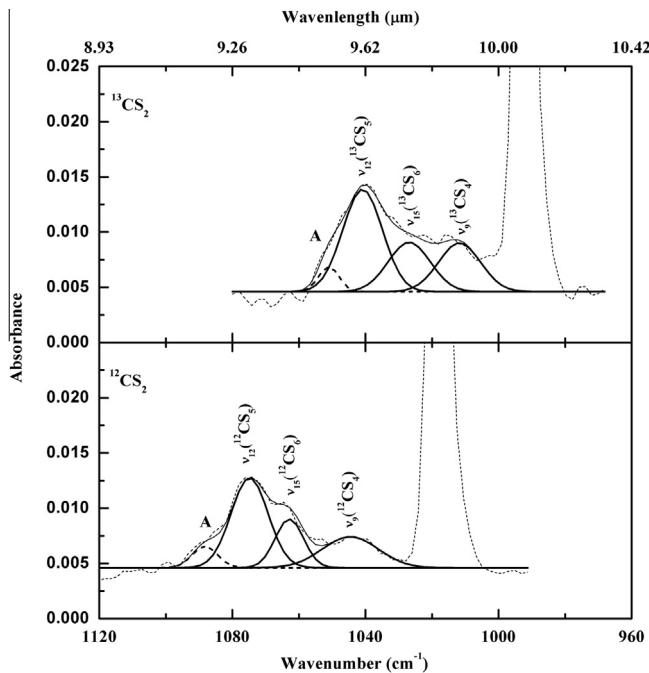


Figure 6. Peak deconvolution of the 1000–1130 cm^{-1} region of irradiated $^{12}\text{CS}_2$ (bottom) and $^{13}\text{CS}_2$ (top) ices (5000 nA).

experiment, $^{13}\text{CS}_4$ (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 $^{12}\text{CS}_4$ (D_{2d}) and $^{13}\text{CS}_4$ (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 vibrational mode of CS_4 (C_{2v}) is calculated at 1141 cm^{-1} after scaling. However, no absorption could be identified in this region.

Further, the absorption feature at 1074 cm^{-1} is attributed to the ν_{12} vibrational mode of the C_2 symmetric carbon pentasulfide iso-

mer CS_5 (1). After scaling, the calculated ν_{12} vibrational mode (CS stretching) of this isomer is 1080 cm^{-1} in good agreement with the observed band. In the irradiated $^{13}\text{CS}_2$ ices, the experimental band is shifted to 1041 cm^{-1} ; this value matches nicely with the computed, scaled ν_{12} vibrational band (CS stretching) at 1046 cm^{-1} . Therefore, on the basis of a consistent agreement of the isotopic shifts of the ν_{12} vibrational modes, the C_2 symmetric carbon pentasulfide isomer CS_5 (1) can be identified. Note that the assigned structure presents the thermodynamically most stable isomer among the calculated structures of carbon pentasulfide.

Finally, the absorption band at 1063 cm^{-1} suggests the formation of a CS_6 isomer. Here, the ν_{15} fundamental band (CS stretching) of the C_2 symmetric carbon hexasulfide isomer CS_6 (1) calculates after scaling to be 1079 cm^{-1} close to the experimental data. The isotopic shift is determined experimentally and theoretically, too. The detection of the ν_{15} band of $^{13}\text{CS}_6$ (C_2) at 1028 cm^{-1} in the $^{13}\text{CS}_2$ experiment is in close agreement with the calculated band at 1046 cm^{-1} after scaling. Note that using recommended scaling factor of 0.956 for MP2/cc-pVQZ level, the calculated ν_{15} vibrational mode of $^{12}\text{CS}_6$ and $^{13}\text{CS}_6$ are calculated to be 1063 and 1031 cm^{-1} , respectively, which are even closer to the experimentally observed bands at 1063 and 1028 cm^{-1} . Therefore, based on the calculated and observed isotopic shifts, we suggest the detection of the most stable, C_2 symmetric CS_6 isomer. Finally, the ratio of the observed and calculated harmonic vibrational frequencies of the CS_x ($x = 3–5$) species and their isotopologues are also calculated (Table 2). The average value of these ratios is calculated to be 0.971 ± 0.005 , which is within the limit of recommended scaling factor of 0.956 ± 0.020 and close to our chosen scaling factor of 0.97.

In order to account for the stability of the assigned CS_x ($x = 4–6$) species, we also monitored the fate of the observed bands (1074– 1045 cm^{-1}) during warm up phase to 300 K. For comparison, neat carbon disulfide sublimes at about 130 K. The absorption band at 1045 cm^{-1} (CS_4 ; D_{2d}) was observed to be stable up to 75 K, when it declined sharply, whereas the other two bands at 1074 cm^{-1} (CS_5 ; C_2), and 1063 cm^{-1} (CS_6 ; C_2) only decreased with the sublimation of the carbon disulfide matrix at 130 K. This clearly indicates the instability of carbon tetrasulfide (CS_4 ; D_{2d}) at

Table 2

The observed positions of the CS_3 , CS_4 , CS_5 , and CS_6 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
$^{12}\text{CS}_3$ (C_{2v})	ν_6	1248	1279	1240	0.975	0.970
$^{13}\text{CS}_3$ (C_{2v})	ν_6	1206	1238	1200	0.974	0.970
$^{12}\text{CS}_4$ (D_{2d})	ν_9	1045	1079	1047	0.968	0.970
$^{13}\text{CS}_4$ (D_{2d})	ν_9	1015	1040	1009	0.976	0.970
$^{12}\text{CS}_5$ (C_2)	ν_{12}	1074	1113	1080	0.965	0.970
$^{13}\text{CS}_5$ (C_2)	ν_{12}	1041	1078	1046	0.966	0.970
$^{12}\text{CS}_6$ (C_2)	ν_{15}	1063	1112	1079 (1063)	0.955	0.970 (0.956)
$^{13}\text{CS}_6$ (C_2)	ν_{15}	1028	1078	1046 (1031)	0.954	0.970 (0.956)

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 1074–1045 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 1100–1000 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 1000 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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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cplett.2013.05.039>.

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