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# Infrared Spectrum of Carbon Trisulfide in Solid Argon

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Cocondensation of carbon disulfide with high-frequency discharged argon at 4 K produced carbon monosulfide and atomic sulfur, which reacted spontaneously upon annealing to form the carbon trisulfide molecule as identified from the multiplets observed in mixed $^{12}$C, $^{13}$C and $^{32}$S, $^{34}$S isotopic spectra. On the basis of isotopic substitution and theoretical frequency calculations, infrared absorptions at 1263.3 and 570.1 cm$^{-1}$ were assigned to predominantly C=S stretching and bending vibrations of $CS_3$ in solid argon. The $CS_3$ molecule, which was calculated to have a singlet ground state with $C_{2v}$ symmetry, dissociated to form the weakly bound SCS−S complex upon visible light irradiation.

## Introduction

The carbon trioxide ($CO_3$) is a reactive intermediate of great significance in combustion, atmospheric, and planetary chemistry,[1] but the isovalent carbon trisulfide molecule has received much less attention. An early kinetics study of the dissociation of carbon disulfide provided indirect evidence for the existence of the $CS_3$ molecule. The decomposition of shock-wave heated carbon disulfide was postulated to proceed via an intermediate step involving the formation of a stable $CS_3$ complex.[2] Subsequent collision experiments using tandem mass spectrometric methodology indicated that carbon trisulfide is a viable molecule in the gas phase.[3] The experimental results also suggested that carbon trisulfide has either $C_{2v}$ or $D_{3h}$ symmetry. Although ab initio MO calculations favor the $C_{2v}$ structure,[4] the experimental results cannot distinguish unequivocally between the $D_{3h}$ and $C_{2v}$ structures. Isotopic labeling studies implied the existence of a second isomer, which was assigned to the chain structure carbon disulfide S-sulfide. The potential energy surfaces of the reaction $S + CS_2 \rightarrow CS_3 \rightarrow CS + S_2$ were investigated by the 6-31G* ab initio self-consistent field method with the inclusion of electron correlation by Møller−Plesset perturbation theory.[4] The triplet reactants and products were predicted to be more stable than their singlet counterparts. The triplet surface contains shallow wells corresponding to the *cis*- and *trans*-$CS_3$ chain structures. The singlet surface involves more strongly bound $CS_3$ complexes, and the carbon trisulfide $C_{2v}$ structure is the most stable one. The singlet chain isomer and the $D_{3h}$ structure are also minima on the potential energy surface, lying only 14.3 and 4.1 kcal/mol higher in energy than the singlet $C_{2v}$ structure. As befits its experimental importance, considerable theoretical effort has been devoted to the electronic structure of $CO_3$, particularly vibronic interactions.[5]

In this article, we report a combined matrix isolation infrared absorption spectroscopic and theoretical study of carbon trisulfide, which was produced via the reaction of carbon monosulfide and atomic sulfur in solid argon. The infrared absorption spectrum of carbon trisulfide is obtained and assigned. In addition, the photodissociation of carbon trisulfide to the weakly bound SCS−S complex is also reported.

## Experimental and Computational Methods

The carbon trisulfide species was prepared by high-frequency discharge in conjunction with matrix isolation. The experimental setup for high-frequency discharge and matrix isolation Fourier transform infrared spectroscopic investigation has been described in detail previously.[6] Briefly, a pure argon gas stream was subjected to discharge from a high-frequency generator (Tesla coil, alternating voltage ranging from 0 to 9 kV, and frequency ranging from 10 to 15 kHz). The resulting beam is mixed with another gas stream containing a $CS_2$/Ar mixture outside the discharge region, followed by codeposition onto the surface of a CsI window cooled normally to 4 K by means of a closed-cycle helium refrigerator. In general, matrix samples were deposited for 1 h at a rate approximately 5 mmol/h for each stream. The infrared absorption spectra of the resulting samples were recorded with a Bruker Vertex 80v spectrometer at 0.5 cm$^{-1}$ resolution between 4000 and 450 cm$^{-1}$ using a DTGS detector. After the infrared spectrum of the initial deposit was recorded, the sample was annealed to different temperatures and cooled back to 4 K for spectral acquisition. Selected samples were also subjected to broad-band irradiation using a tungsten lamp with glass filters. The $CS_2$/Ar (1:1000) mixtures were prepared in a stainless steel vacuum line using standard manometric techniques. $^{13}CS_2$ and $C^{34}S_2$ (Isotec, 99%) were used without further purification in different experiments.

Complementary spectra were also obtained after codeposition of laser-ablated metal atoms and $CS_2$ in excess argon using methods described previously.[7] In this case, the laser ablation plume provides an intense source of ultraviolet light to irradiate the condensing matrix sample. These samples were annealed to allow diffusion and reaction of trapped atoms and molecules. In particular, two different isotopic mixtures were employed, a mechanical mixture of $C^{32}S_2 + C^{34}S_2$ and such a mixture discharged in a pyrex bulb, which contained $C^{32}S_2 + C^{32}S^{34}S + C^{34}S_2$.

Ab initio and density functional theory calculations were performed to predict the structure and vibrational frequencies

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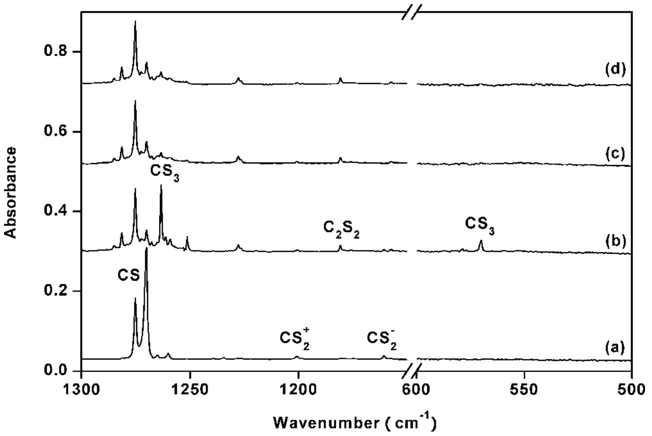

**Figure 1.** Infrared spectra in the 1300−1150 and 600−500 cm$^{-1}$ regions from codeposition of 0.1% $CS_2$/Ar with high-frequency discharged argon. (a) After 1 h of sample deposition at 4 K, (b) after 28 K annealing, (c) after 15 min of $\lambda > 500$-nm irradiation, and (d) after 28 K annealing.

of the experimentally observed species using the Gaussian 03 program.[8] The ab initio calculations were performed at the MP2 level of theory, and the density functional theory calculations were performed using the three-parameter hybrid functional according to Becke with additional correlation corrections due to Lee, Yang, and Parr (B3LYP).[9] The 6-311+G* basis set was used for both the C and S atoms.[10] The geometries were fully optimized at both levels of theory. The harmonic vibrational frequencies were calculated, and zero-point vibrational energies were derived. Transition-state optimizations were done with the synchronous transit-guided quasi-Newton method at the MP2/6-311+G* level.[11] The IRC calculations were performed to verify the transition states connecting the reactant and product on the potential energy surface.

## Results and Discussion

Microwave or high-frequency discharge has often been used in conjunction with the matrix isolation technique to produce and trap unstable species for spectroscopic studies. The products from condensation of $CS_2$/Ar with microwave or high-frequency discharged argon have been investigated previously by several groups.[12−14] The product absorptions depend strongly on the power levels of the discharge. With quite a high power of discharge, the $CS_2$ molecules dissociate readily to form the CS molecules, which were observed at 1275.0 and 1270.0 cm$^{-1}$ in solid argon. Sample annealing allows the fragments to diffuse and react to form the $C_2S_2$ (1180.5 cm$^{-1}$) and $C_3S_2$ (2078.2 and 1024.3 cm$^{-1}$) molecules.[13] When the experiment was performed with very low power of discharge, the CS absorption was weak, whereas the charged species including $CS_2^+$ (1200.5 cm$^{-1}$), $CS_2^-$ (1160.5 cm$^{-1}$), $(CS_2)_2^+$ (1379.7 cm$^{-1}$), and $(CS_2)_2^-$ (909.0 cm$^{-1}$) became obvious.[7,15−17] The present experiments employ medium discharge power. The spectra in selected regions are shown in Figure 1. The CS absorptions dominate the spectrum after sample deposition, but weak absorptions due to $CS_2^+$ and $CS_2^-$ were also observed. When the sample was annealed to 28 K (Figure 1, trace b), the CS absorption (mainly the 1270.0 cm$^{-1}$ site) decreased with the formation of the $C_2S_2$ absorption and a group of new absorptions at 1263.3, 1251.5, 1100.7, and 570.1 cm$^{-1}$. These absorptions were destroyed when the sample was subjected to broad-band irradiation by a tungsten lamp with a $\lambda > 500$-nm-long wavelength pass filter. The difference spectrum shown in Figure 2 (spectrum taken after 15 min of $\lambda > 500$-nm irradiation minus spectrum taken right after 28 K annealing) clearly shows that a sharp absorption at 1523.7 cm$^{-1}$ appeared with the disappearance of the 1263.3 cm$^{-1}$ absorption upon irradiation. The 1263.3, 1251.5, 1100.7, and 570.1 cm$^{-1}$ absorptions were not recovered under subsequent sample annealing (Figure 1, trace d).

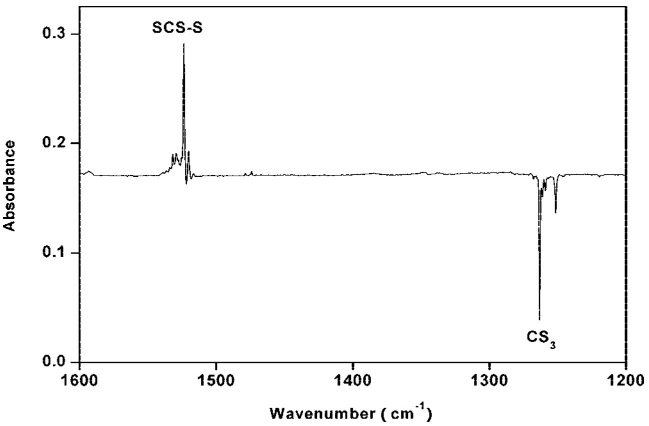

**Figure 2.** Difference IR spectra in the 1600−1200 cm$^{-1}$ region from codeposition of 0.1% $CS_2$/Ar with high-frequency discharged argon at 4 K (spectrum taken after 15 min of $\lambda > 500$-nm irradiation minus spectrum taken after 28 K annealing of the as-deposited sample).

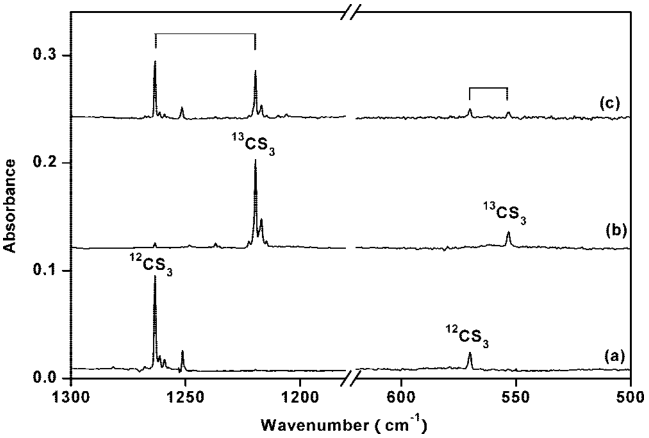

**Figure 3.** Difference IR spectra in the 1300−1180 and 620−500 cm$^{-1}$ regions (spectrum taken after 28 K annealing minus spectrum taken after 15 min of $\lambda > 500$-nm irradiation) from (a) 0.1% $^{12}CS_2$/Ar, (b) 0.1% $^{13}CS_2$/Ar, and (c) 0.05% $^{12}CS_2$ + 0.05% $^{13}CS_2$/Ar.

Similar experiments were repeated with the $^{13}CS_2$/Ar, $C^{34}S_2$/Ar, $^{12}CS_2$ + $^{13}CS_2$/Ar, and $C^{32}S_2$ + $C^{34}S_2$/Ar samples. The difference IR spectra in selected regions with different isotopic samples are shown in Figures 3 and 4.

The complementary laser-ablated metal experiments with argon/$C^{32}S_2$ (0.2%) samples produced a new 1263.3 cm$^{-1}$ absorption on annealing the samples to 20 K, which increased stepwise at the expense of CS absorptions[11] on further annealing to 30, 35, and 40 K with intensities reaching 0.005−0.010 absorbance units. This band position was independent of the metal employed. Similar experiments with an argon/$C^{34}S_2$ sample shifted the major new absorption to 1255.5 cm$^{-1}$. A number of investigations with the $C^{32}S_2$ + $C^{34}S_2$ mixed isotopic sample produced a quintet of absorptions at 1263.3, 1261.1, 1259.2, 1257.1, and 1255.5 cm$^{-1}$ on sample annealing. The reagent spectrum revealed a very strong triplet absorption at 1528.1, 1524.6, and 1521.1 cm$^{-1}$ with the middle peak for $C^{32}S^{34}S$ weaker than the outer bands for $C^{32}S_2$ + $C^{34}S_2$. This indicates some precursor reformation during sample deposition

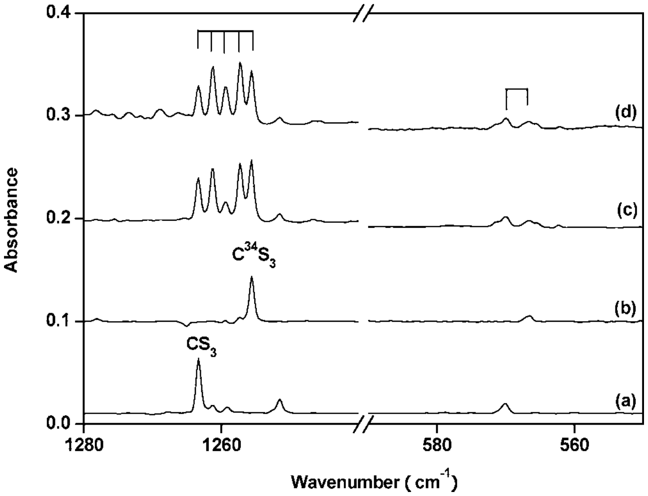

**Figure 4.** Difference IR spectra in the 1280−1240 and 590−550 cm$^{-1}$ regions (spectrum taken after 28 K annealing minus spectrum taken after 15 min of $\lambda$ > 500-nm irradiation) from (a) 0.1% $C^{32}S_2$/Ar, (b) 0.1% $C^{34}S_2$/Ar, (c) 0.1% $C^{32}S_2$ + 0.1% $C^{34}S_2$/Ar with low power of discharge, and (d) 0.1% $C^{32}S_2$ + 0.1% $C^{34}S_2$/Ar with high power of discharge.

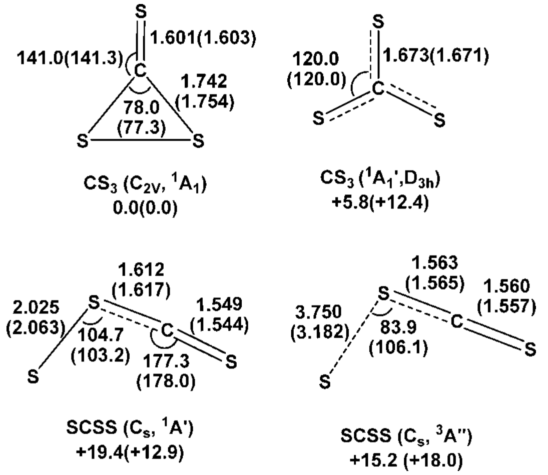

**Figure 5.** Optimized structures (bond lengths in angstroms; bond angles in degrees) and relative stabilities (kilocalories per mole) of various $CS_3$ isomers at the MP2 and B3LYP (values in parentheses) levels of theory.

from the CS + S reaction. When the precursor isotopic mixture was discharged, the 1524.6 cm$^{-1}$ band was relatively stronger and the 1261.1 and 1257.1 cm$^{-1}$ product absorptions were also relatively stronger than the other three mixed isotopic product absorptions. Finally, laser-ablated metal experiments with the carbon-13 substituted precursor shifted the band growing in on annealing to 1219.3 cm$^{-1}$.

Similar laser ablation experiments were done in excess neon, and the product bands were weaker. The neon matrix counterparts were observed at 1268.2, 1260.8, and 1223.4 cm$^{-1}$ for the $C^{32}S_2$, $C^{34}S_2$, and $^{13}C^{32}S_2$ reaction products, respectively.

**$CS_3$.** The absorptions at 1263.3, 1251.5, 1100.7, and 570.1 cm$^{-1}$ appeared together on annealing at the expense of the CS absorption. The 1263.3 cm$^{-1}$ absorption shifted to 1219.4 cm$^{-1}$ with a $^{13}CS_2$/Ar sample and shifted to 1255.5 cm$^{-1}$ when a $C^{34}S_2$ sample was used. The $^{12}C/^{13}C$ isotopic frequency ratio of 1.0360 is slightly higher than those of antisymmetric CS stretching mode of $CS_2$ and $CS_2^-$. Only the 1263.3 and 1219.3 cm$^{-1}$ absorptions were observed in the spectrum from the experiment with an equal molar mixture of $^{12}CS_2$ and $^{13}CS_2$ (Figure 3, trace c), indicating that only one C atom is involved in this vibrational mode. In the experiments with an equal molar mixture of $C^{32}S_2$ and $C^{34}S_2$, a quintet at 1263.3, 1261.1, 1259.2, 1257.1, and 1255.5 cm$^{-1}$ was observed (Figure 4, traces c and d). The relative intensities of the intermediate absorptions increased with respect to the 1263.3 and 1255.5 cm$^{-1}$ absorptions in the experiment using relatively high power of discharge with increased isotopic mixing (Figure 4, trace d). The mixed isotopic spectral features suggest that the absorber involves two equivalent sulfur atoms and one more nonequivalent sulfur atom. (A vibrational mode that involves three sulfur atoms with two of them being equivalent will split into six absorptions with a mixture of $C^{32}S_2/C^{32}S^{34}S/C^{34}S_2$; the observed 1259.2 cm$^{-1}$ intermediate band probably contains two unresolved absorptions.) The 570.1 cm$^{-1}$ absorption showed a 16.8 cm$^{-1}$ carbon-13 isotopic shift. The spectrum with the mixed $^{12}CS_2$ + $^{13}CS_2$/Ar sample also indicated the involvement of only one C atom in this mode. This absorption shifted to 566.5 cm$^{-1}$ with $C^{34}S_2$, and only two broad absorptions were observed in the experiments with the $C^{32}S_2$ + $C^{34}S_2$ mixture. These two absorptions are appropriate for the CS stretching and bending vibrations of carbon trisulfide, $CS_3$. (The low mode was assigned to the antisymmetric $CS_2$ stretching mode in the literature,[4] and it is better to be described as a coupled CS bending, antisymmetric $CS_2$ stretching mode based upon the observed isotopic splitting). The much weaker 1100.7 cm$^{-1}$ absorption exhibited about the same isotopic frequency ratios as those of the 570.1 cm$^{-1}$ absorption and is assigned to the overtone of the 570.1 cm$^{-1}$ absorption. The 1251.5 cm$^{-1}$ absorption shifted to 1216.8 cm$^{-1}$ with $^{13}CS_2$. The counterpart with $C^{34}S_2$ was not observed, suggesting that it is not due to a site absorption of the 1263.3 cm$^{-1}$ band. It could be due to a combination mode that is in Fermi resonance with the strong CS stretching fundamental.

The geometry and vibrational frequencies of $CS_3$ were previously addressed by Froese and Goddard by using ab initio calculations at the MP2 level of theory.[4] These calculations predicted that carbon trisulfide may exist with either $C_{2v}$ or $D_{3h}$ symmetry. The $D_{3h}$ structure was predicted to be 4.1 kcal/mol higher in energy than the $C_{2v}$ structure. The scaled harmonic frequencies for the $C_{2v}$ structure were reported at 1227 and 584 cm$^{-1}$, which are in excellent agreement with the anharmonic frequencies observed in solid argon. We also carried out theoretical calculations at both the B3LYP/6-311+G* and MP2/6-311+G* levels of theory. We performed geometric optimizations on both the $C_{2v}$ and $D_{3h}$ structures, and the optimized structures are shown in Figure 5. Both structures were computed to be minima on the singlet potential energy surface. At both levels of theory, the $C_{2v}$ structure was predicted to be more stable than the $D_{3h}$ isomer by about 12.4 (B3LYP) or 5.8 kcal/mol (MP2). The $C_{2v}$ structure of $CS_3$ is similar to the previously reported $CO_3$, $OCS_2$, and $SCH_2$ analogous molecules, which were also determined to have $C_{2v}$ structures.[12,18−20]

The calculated harmonic vibrational frequencies of the $C_{2v}$ structure of the $CS_3$ molecule are compared with the experimental values in Table 1. The carbon trisulfide molecule with $C_{2v}$ symmetry possesses six vibrational modes that are all IR active. Both the CS stretching and bending modes were predicted to have appreciable IR intensities (Table 1) and should be observed experimentally. The other four modes were predicted to have very low IR intensities (less than 3 km/mol) and cannot be observed in the present experiments. At the MP2 level of theory, the CS stretching vibrational mode was predicted at 1282.2 cm$^{-1}$ with the $^{12}C/^{13}C$ and $^{32}S/^{34}S$ isotopic frequency ratios of 1.0337 and 1.0050, respectively, which are in reason-

**TABLE 1: Comparison of the Calculated and Observed Vibrational Frequencies (cm$^{-1}$) and Intensities (km/mol, in Parentheses) for the Carbon Trisulfide ($CS_3$)**

| calcd[a] | | | | obsd[b] | | | |
|---|---|---|---|---|---|---|---|
| MP2 | | | B3LYP | | | | |
| $^{12}C^{32}S_3$ | $^{13}C^{32}S_3$ | $C^{34}S_3$ | $C^{32}S_3$ | $^{12}C^{32}S_3$ | $^{13}C^{32}S_3$ | $C^{34}S_3$ | mode |
| 1282.2 (398) | 1240.4 (370) | 1275.8 (396) | 1224.7 (465) | 1263.3 (1.00) | 1219.4 | 1255.5 | CS stretch |
| 617.3 (60) | 598.0 (57) | 613.7 (59) | 574.4 (60) | 570.1 (0.33) | 553.3 | 566.5 | CS bend, $CS_2$ antisym. stretch |
| 581.6 (5) | 581.4 (5) | 564.4 (5) | 570.1 (2) | | | | CS stretch, $CS_2$ sym. stretch |
| 401.6 (5) | 400.8 (5) | 390.2 (5) | 401.9 (3) | | | | $CS_2$ scissor |
| 390.9 (4) | 377.3 (3) | 389.5 (4) | 393.8 (2) | | | | out-of-plane wag. |
| 292.7 (1) | 291.7 (1) | 284.7 (1) | 278.2 (2) | | | | CS bend, $CS_2$ rock |

[a] The “CS stretching mode” red shifts for the mixed 32,34 isotopic molecules are compared for MP2 calculations and argon matrix observations: 32 = C-32,34 [0.6 cm$^{-1}$ calcd, 2.2 cm$^{-1}$ obsd], 32 = C-34,34 [1.2, 4.0], 34 = C-32,32 [5.1, 4.0], 34 = C-32,34 [5.7, 6.2]. The CCSD(T) method predicted the three highest frequencies at 1252, 634, and 569 cm$^{-1}$. The $CS_3$ molecule with $D_{3h}$ structure was predicted to have vibrations at 1280.6 cm$^{-1}$ (1963 × 2 km/mol), 555.3 cm$^{-1}$ (0 km/mol), 378.0 cm$^{-1}$ (10 km/mol), and 374.8 cm$^{-1}$ (107 × 2 km/mol) at the MP2 level of theory. [b] Argon matrix: Integrated intensity normalized to the most intense absorption.

able agreement with the experimental values of 1.0360 and 1.0062. However, with purely mechanical interactions, an increased ratio for one isotope is usually met by a decreased ratio for the other as these two atoms participate in the normal vibrational mode that is not perfectly described by the calculation. The CS bending mode was calculated at 617.3 cm$^{-1}$ with the $^{12}C/^{13}C$ and $^{32}S/^{34}S$ isotopic frequency ratios of 1.0323 and 1.0059, which are close to the experimental values of 1.0304 and 1.0064. Taking the anharmonicity and matrix shift into consideration, both modes are underestimated at the B3LYP level of theory. Similar frequency underestimation has also been reported for some other sulfur-containing compounds.[21,22]

It is of more concern that the mixed sulfur-32,34 isotopic shifts are underestimated considerably by the MP2 calculations (see footnote in Table 1). In other words, the two bridged sulfur atoms participate more in the C═S stretching mode than is modeled by harmonic calculations. Very recent electronic structure calculations on $CO_3$ using equation of motion and coupled-cluster methods reveal considerable vibronic interactions with low-lying electronic states, which have strong effects on the ground-state structure and vibrational frequencies.[5] We believe that similar vibronic interactions are evidenced for $CS_3$ in the isotopic shifts, first in the observation of both more $^{13}C$ and $^{34}S$ shift than the calculated harmonic values, and second in the observation of more mixing of the two bridged sulfur atoms with the terminal C═S vibrational mode than is described by the harmonic calculation.

The carbon trisulfide intermediate has previously been prepared by electron impact ionization of 4,5-dioxo-2-thioxo-1,3-dithiolan and detected by neutralization reionization mass spectrometry.[3] The experimental results suggest that the neutral carbon trisulfide may exist as either $C_{2v}$ or $D_{3h}$ structures. However, the experimental results cannot distinguish unequivocally between the $D_{3h}$ and $C_{2v}$ structures. As has been mentioned above, the $D_{3h}$ structure was predicted to be less stable than the $C_{2v}$ isomer. Of more importance, the calculated frequencies also support the assignment of the observed absorptions in solid argon to the $C_{2v}$ structure instead of the $D_{3h}$ isomer. The $D_{3h}$ structure was predicted to have six vibrational modes. The doubly degenerate antisymmetric CS stretching mode was predicted to be the most intense absorption, which was located at 1280.6 cm$^{-1}$ at the MP2 level. Although the frequency of this mode is very close to that of the $C_{2v}$ structure, the calculation predicted that there is no other IR active absorption above 400 cm$^{-1}$ for the $D_{3h}$ structure. (The symmetric CS stretching mode of the $D_{3h}$ structure was predicted at 555.3 cm$^{-1}$, but this mode is IR inactive.) Apparently, the observed infrared absorptions in the present experiments are due to the carbon trisulfide molecule with the $C_{2v}$ structure in solid argon. The complementary observation of the major band for $CS_3$ using the different method of laser ablation (plume irradiation) adds support for this assignment. In addition, the small 5 cm$^{-1}$ neon matrix blue shift observed for this band verifies that there is no unusual matrix effect on the guest molecule.[23]

**SCS−S.** The difference spectrum shown in Figure 2 clearly shows that the $CS_3$ absorptions disappeared upon $\lambda > 500$-nm irradiation. In concert, a new absorption at 1523.7 cm$^{-1}$ was produced. The band center of this absorption is only 4.6 cm$^{-1}$ red-shifted from the antisymmetric CS stretching vibration of $CS_2$ molecule observed at 1528.3 cm$^{-1}$ in solid argon. The $^{13}C$ and $^{34}S$ counterparts were observed at 1474.7 and 1516.6 cm$^{-1}$ with the observed carbon-13 and sulfur-34 isotopic shift (49.0 and 7.1 cm$^{-1}$) very close to those of the antisymmetric CS stretching mode of $CS_2$. This suggests that the 1523.7 cm$^{-1}$ absorption is due to an antisymmetric CS stretching mode of a weakly perturbed $CS_2$. On the basis of the observed photoconversion relationship between the 1523.7 cm$^{-1}$ absorption and the $CS_3$ absorptions, we assign the 1523.7 cm$^{-1}$ absorption to the antisymmetric CS stretching mode of a SCS−S complex.

Theoretical calculations were performed on the SCS−S complex to support the experimental assignment. Geometry optimizations were performed on both the singlet and triplet spin states starting from the SCSS rearrangement. At the B3LYP level of theory, geometry optimization on the singlet state converged to the bent carbon disulfide S-sulfide structure with a S−S bond length of 2.063 Å, in agreement with a previous report.[4] Geometry optimization on the triplet state found a very weakly bound SCS−S complex structure with a S−S distance of 3.182 Å to be lowest in energy. Similar structures were obtained at the MP2 level of theory, as shown in Figure 5. The singlet carbon disulfide S-sulfide structure is 5.1 kcal/mol more stable than the triplet-state SCS−S complex with B3LYP. However, the triplet state weakly bound complex was predicted to be 4.2 kcal/mol more stable than the singlet-state carbon disulfide S-sulfide structure at the MP2 level of theory. The calculated vibrational frequencies (Table 2) also support the assignment of the 1523.7 cm$^{-1}$ to the triplet state weakly bound SCS−S complex instead of the carbon disulfide S-sulfide structure previously predicted.[4] At the B3LYP level, the triplet-state SCS−S complex was predicted to have a very strong antisymmetric CS stretching vibration at 1544.4 cm$^{-1}$, about 9.6 cm$^{-1}$ red-shifted from that of $CS_2$ calculated at the same level of theory. The same mode of the singlet-state carbon disulfide S-sulfide was predicted at 1485.9 cm$^{-1}$, too low to fit

**TABLE 2: Comparison between the Calculated and Observed Vibrational Frequencies ($cm^{-1}$) and Intensities (km/mol, in Parentheses) for the SCS−S Complex**

| calcd | | | | | | | |
|---|---|---|---|---|---|---|---|
| MP2 | | | B3LYP | exptl | | | |
| $^{12}C^{32}S_3$ | $^{13}C^{32}S_3$ | $C^{34}S_3$ | $C^{32}S_3$ | $^{12}C^{32}S_3$ | $^{13}C^{32}S_3$ | $C^{34}S_3$ | assignment |
| 1636.7 (552) | 1582.6 (516) | 1629.1 (547) | 1544.4 (780) | 1523.7 | 1474.7 | 1516.5 | S=C=S asym. stretch |
| 683.9 (0.03) | 683.9 (0.03) | 663.5 (0.03) | 671.9 (0.1) | | | | S=C=S sym. stretch |
| 372.1 (5) | 359.8 (5) | 370.4 (5) | 395.2 (2) | | | | S=C=S bend |
| 370.4 (5) | 358.1 (4) | 368.6 (5) | 394.7 (4) | | | | S=C=S bend |
| 50.8 (0.2) | 50.8 (0.2) | 49.4 (0.2) | 60.7 (6) | | | | S−S stretch |
| 18.8 (0.03) | 18.8 (0.03) | 18.2 (0.03) | 29.6 (0.1) | | | | C=S−S bend |

[a] The $CS_2$ molecule was predicted to have vibrations at 1637.3, 684.1, and 371.1 $cm^{-1}$ (MP2) or 1554.0, 673.9, and 397.5 $cm^{-1}$ (B3LYP).

the observed value. At the MP2 level of theory, the antisymmetric CS stretching vibration of the SCS−S complex was predicted at 1636.7 $cm^{-1}$, about 0.6 $cm^{-1}$ lower than that of $CS_2$ calculated at the same level. The frequency shift upon the S atom perturbation is underestimated by MP2 but is overestimated by B3LYP. The SCS antisymmetric stretching mode of the carbon disulfide S-sulfide structure calculated to be 1558 $cm^{-1}$ at the MP2/6-31G* level of theory is about 80 $cm^{-1}$ lower than the antisymmetric stretching mode of $CS_2$ calculated at the same level of theory.[4]

**Reaction Mechanisms.** Cocondensation of $CS_2$/Ar with high-frequency discharged argon produced carbon monosulfide as well as sulfur atoms. On the basis of the experimental observations, the $CS_3$ molecules were formed via the reactions of carbon monosulfide with sulfur atoms or disulfur molecules upon sample annealing in solid argon. According to the MP2 calculations, the reaction of ground-state CS and $S_2$ to form $CS_3$ is exothermic by 35.7 kcal/mol. If the reaction proceeded via CS and two sulfur atoms, the association reaction would be even more exothermic.

$$CS(^1\Sigma) + S_2(^3\Sigma_g) \rightarrow CS_3(^1A_1) \quad \Delta E = -35.7 \text{ kcal/mol} \tag{1}$$

The carbon trisulfide absorptions disappeared under $\lambda > 500$-nm irradiation, during which the SCS−S complex absorption was produced. This observation implies that visible light initiates dissociation reaction 2 to give the carbon disulfide molecule and sulfur atom. The in situ formed $CS_2$ and S fragments cannot escape the matrix "cage" and survive as the weakly bound SCS−S complex in solid argon. The SCS−S complex was predicted to be only 1.1 kcal/mol lower in energy than the separated $CS_2$ and S.

$$CS_3(^1A_1) \rightarrow SCS{-}S(^3A'') \quad \Delta E = 16.3 \text{ kcal/mol} \tag{2}$$

The complementary laser-ablated metal experiments with $CS_2$ provide support for the above assignments and another reaction mechanism since a substantial amount $CS_2$ remains in these samples as a reagent molecule. The observation of CS in these expermiments also attests to the formation of S atoms by the photophysical effect of the laser ablation plume. The appearance and growth of the strongest new product absorption on annealing to 20−40 K in solid argon is in agreement with the above mechanism. However, the increased yield of the mixed isotopic bands at 1261.0 and 1257.0 $cm^{-1}$ when the reagent contains a higher proportion of $C^{32}S^{34}S$ suggests that these two bands are due to the $^{32}SC^{32}S^{34}S$ and $^{34}SC^{32}S^{34}S$ isotopic molecules and that excited S atom reaction 3 contributes to the overall reaction yield during deposition in the laser ablation experiments. Reactions of S atoms in matrixes have been discussed previously.[24]

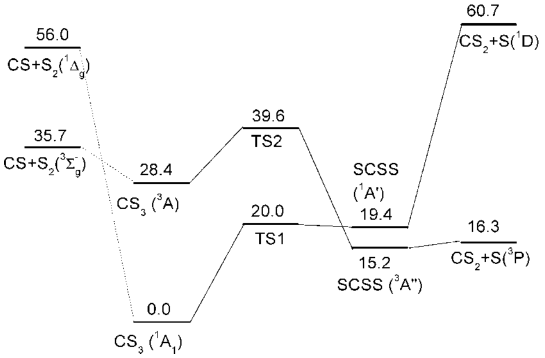

**Figure 6.** Potential energy profiles for the CS + $S_2$ reaction calculated at the MP2/6-311++G** level of theory (values are given in kcal/mol). The dashed line indicates the computationally unexplored spin-crossing area.

$$CS_3(^1A_1) + S(^1D) \rightarrow CS_3(^1A_1) \tag{3}$$

The potential energy profiles of the CS + $S_2$ → $CS_2$ + S reaction calculated at the MP2 level of theory are shown in Figure 6. The $S_2$ molecule has a triplet ground state, while the $CS_3$ molecule has a singlet ground state. Therefore, the process from CS and $S_2$ to give $CS_3$ involves spin-crossing. From singlet $CS_3$, one of the cyclic C−S bonds is broken to form the carbon disulfide S-sulfide isomer which was predicted to be 19.4 kcal/mol less stable than the singlet $C_{2v}$ $CS_3$ isomer. This process proceeds via a transition state (TS1) lying 20.0 kcal/mol above the singlet $CS_3$ structure. The carbon sulfide S-sulfide intermediate dissociates to give $CS_2$ and singlet ($^1$D) S atom. Since the triplet SCS−S complex is 4.2 kcal/mol lower in energy than the singlet carbon sulfide S-sulfide structure, there is another spin-crossing between triplet and singlet potential energy surfaces from $CS_3$ to the SCS−S complex. The overall reaction from CS + $S_2$ to form $CS_2$ + S was predicted to be exothermic by 19.4 kcal/mol, and spin-crossing occurs twice between the singlet and triplet potential energy surfaces. The theoretical calculation results imply that the $CS_3$ molecule with $C_{2v}$ symmetry is an important intermediate in the CS + $S_2$ → $CS_2$ + S and its reverse reactions, as also has been suggested by previous reports,[3,4] which is in accord with the present experimental observations.

The potential energy profiles shown in Figure 6 also suggest that the reaction between ground-state $CS_2$ molecule and atomic sulfur in forming the carbon trisulfide intermediate is exothermic but has an energy barrier of 3.7 kcal/mol. Consistent with the calculation results, we found that the SCS−S complex photochemically formed from $CS_3$ is not able to rearrange back to the $CS_3$ intermediate spontaneously on annealing. Previous laser-induced fluorescence studies in the gas phase showed that singlet $^1D$ excited-state atomic sulfur is able to react with the ground-state $CS_2$ molecule to give CS and $S_2$ in its triplet electronic ground state,[25] which was predicted to be exothermic by more than 20 kcal/mol based on present MP2 calculations.

## Conclusions

Cocondensation of $CS_2$/Ar with high-frequency discharged argon produced carbon monosulfide as well as sulfur atoms. Sample annealing allows the fragments to diffuse and react to form the carbon trisulfide molecule, which was identified from the multiplets observed in mixed $^{12}C$, $^{13}C$ and $^{32}S$, $^{34}S$ isotopic spectra. On the basis of isotopic substitution as well as theoretical frequency calculations, infrared absorptions at 1263.3 and 570.1 cm$^{-1}$, which were produced spontaneously in solid argon on annealing, are assigned to the predominantly C=S stretching and bending vibrations of $CS_3$. The carbon trisulfide molecule was calculated to have a singlet ground state with $C_{2v}$ symmetry. Vibronic interactions in the ground-state molecule are evidenced by the vibrational isotopic shifts.

Under visible light irradiation, the $CS_3$ molecule dissociated to form the weakly bound SCS−S complex, which was predicted to be more stable than the carbon disulfide S-sulfide isomer. Both experimental observation and theoretical calculation results imply that the $CS_3$ molecule is an important intermediate in the $CS + S_2 \rightarrow CS_2 + S$ reaction and its reverse.

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## References and Notes

(1) (a) Froese, R. D. J.; Goddard, J. D. *J. Chem. Phys.* **1993**, *97*, 7483. (b) Mebel, A. M.; Hayashi, M.; Kislov, V. V.; Lin, S. H. *J. Phys. Chem. A* **2004**, *108*, 7983. (c) Jamieson, C. S.; Mebel, A. M.; Kaiser, R. I. *Comput. Phys. Chem.* **2006**, *7*, 2508.

(2) Arnold, S. J.; Brownlee, W. G.; Kimbell, G. H. *J. Phys. Chem.* **1970**, *74*, 8.

(3) Sulzle, D.; Egsgaard, H.; Carlsen, L.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 3750.

(4) Froese, R. D. J.; Goddard, J. D. *J. Chem. Phys.* **1992**, *96*, 7449.

(5) Kowalczyk, T.; Krylov, A. I. *J. Phys. Chem. A* **2007**, *111*, 8271.

(6) (a) Ma, R. H.; Yuan, D. M.; Chen, M. H.; Zhou, M. F. *J. Phys. Chem. A* **2009**, *113*, 1250. (b) Wang, G. J.; Zhou, M. F. *Int. Rev. Phys. Chem.* **2008**, *27*, 1.

(7) (a) Zhou, M. F.; Andrews, L. *J. Chem. Phys.* **2000**, *112*, 6576. (b) Zhou, M. F.; Andrews, L. *J. Phys. Chem. A* **2000**, *104*, 4394. (c) Baker, A. B.; Andrews, L. *J. Phys. Chem. A* **2006**, *110*, 12785.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004.

(9) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(10) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (b) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(11) Head-Gordon, M.; Pople, J. A.; Frisch, M. *Chem. Phys. Lett.* **1988**, *153*, 503.

(12) (a) Jacox, M. E.; Milligan, D. E. *J. Mol. Spectrosc.* **1975**, *58*, 142. (b) Takeuchi, H.; Tasumi, M. *J. Mol. Spectrosc.* **1981**, *90*, 116.

(13) Bohn, R. B.; Hannachi, Y.; Andrews, L. *J. Am. Chem. Soc.* **1992**, *114*, 6452.

(14) (a) Kong, Q. Y.; Zeng, A. H.; Chen, M. H.; Zhou, M. F.; Xu, Q. *J. Chem. Phys.* **2003**, *118*, 7267. (b) Kong, Q. Y.; Zeng, A. H.; Chen, M. H.; Xu, Q.; Zhou, M. F. *J. Phys. Chem. A* **2004**, *108*, 1531. (c) Zhou, M. F.; Kong, Q. Y.; Jin, X.; Zeng, A. H.; Chen, M. H.; Xu, Q. *J. Phys. Chem. A* **2004**, *108*, 11014.

(15) (a) Bondybey, V. E.; English, J. H.; Miller, T. A. *J. Chem. Phys.* **1979**, *70*, 1621. (b) Bondybey, V. E.; English, J. H. *J. Chem. Phys.* **1980**, *73*, 3098.

(16) Halasinski, T. M.; Godbout, J. T.; Allison, J.; Leroi, G. E. *J. Phys. Chem.* **1996**, *100*, 14865.

(17) Yu, L.; Zeng, A. H.; Xu, Q.; Zhou, M. F. *J. Phys. Chem. A* **2004**, *108*, 8264.

(18) Weissberger, E.; Breckenridge, W. H.; Taube, H. *J. Chem. Phys.* **1967**, *47*, 1764.

(19) Lo, W. J.; Chen, H. F.; Chou, P. H.; Lee, Y. P. *J. Chem. Phys.* **2004**, *121*, 12371.

(20) Torres, M.; Safarik, I.; Clement, A.; Strausz, O. P. *Can. J. Chem.* **1982**, *60*, 1187.

(21) Ulic, S. E.; Ahsen, S. V.; Willner, H. *Inorg. Chem.* **2004**, *43*, 5268.

(22) (a) Zeng, A. H.; Yu, L.; Wang, Y.; Kong, Q. Y.; Xu, Q.; Zhou, M. F. *J. Phys. Chem. A* **2004**, *108*, 6656. (b) Chen, M. H.; Yang, R. J.; Ma, R. H.; Zhou, M. F. *J. Phys. Chem. A* **2008**, *112*, 7157.

(23) Jacox, M. E. *Chem. Phys.* **1994**, *189*, 149.

(24) (a) Long, S. R.; Pimentel, G. C. *J. Chem. Phys.* **1977**, *66*, 2219. (b) Smardzewski, R. R. *J. Chem. Phys.* **1978**, *68*, 2878.

(25) Sapers, S. P.; Andraos, N.; Donaldson, D. J. *J. Chem. Phys.* **1991**, *95*, 1738.

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