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Production and Reactions of Triplet CS: Matrix Infrared and Ultraviolet Spectra of C_2S_2[†]

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Abstract: Matrix infrared and visible–ultraviolet absorption spectroscopy and ab initio electronic structure calculations have been used to characterize the reaction products from a Tesla coil Ar/CS_2 discharge. The discharge is an excellent source of CS, which reacts with other molecules to form the major C_3S_2 product and the transient C_2S_2 species. The spectra of discharged mixed isotopic samples Ar/$^{12}CS_2$/$^{13}CS_2$ and Ar/$C^{32}S_2$/$C^{34}S_2$ exhibit triplet patterns in the CS antisymmetric stretching region, which unambiguously identifies the new C_2S_2 molecule with two equivalent CS subgroups. The magnitudes of the ^{12,13}C and ^{32,34}S isotopic shifts further characterize the diatomic CS subgroup nature of C_2S_2. Another product contains two equivalent CS subgroups interacting with inequivalent S atom(s). The formation of C_2S_2 ($^3\Sigma$) from the simple CS_2 discharge requires triplet CS. Evidence was also obtained for other transient cumulene species.

Introduction

Carbon and sulfur are among the most abundant atoms in the universe. The simplest molecule containing these atoms is diatomic CS, which is closely related to CO. Large cumulene compounds containing both carbon and sulfur, with the general formula C_nS_2 and sulfur atoms in terminal positions, have been detected in the interstellar medium.[1] Two well-known cumulenes on Earth are CS_2 and C_3S_2. The latter, a red, oily liquid, was first prepared in 1893 by passing Ar/CS_2 through an electrical discharge.[2] In more recent studies, the phosphorescence spectrum of C_3S_2 has been observed from samples formed by condensing a discharged Ar/CS_2 stream.[3] The C_2 cumulene, C_2S_2, has not been isolated in the laboratory nor observed in the interstellar environment. However, theoretical calculations by Schaefer et al. predict a stable, linear, centrosymmetric structure for the triplet ground state C_2S_2 molecule.[4] Experimental evidence for the existence of C_2S_2 has been offered by very recent neutralization–reionization mass spectrometry as well as matrix photochemical and flash vacuum pyrolysis studies using complicated bicyclic $C_xS_yO_z$ precursors.[5-7] A preliminary account of the present CS_2 discharge work and observation of C_2S_2 has been presented.[8] The purpose of this investigation was to characterize the products of Tesla coil Ar/CS_2 discharges, particularly triplet CS reaction products. It was desired to prepare C_2S_2 from the simplest possible reagent and to characterize the chemistry of carbon and sulfur atoms produced in electrical discharges, which are representative of atmospheric and outer space environments. These experiments also demonstrate the strength and value of the matrix isolation technique as well as its usefulness in solving chemical problems of planetary significance.

Experimental Section

Ar/CS_2 mixtures (matrix reagent = M/R) of 50/1 or 100/1 were prepared in a stainless steel vacuum line using standard manometric techniques. CS_2 (Merck) was cooled to 77 K using liquid N_2 and evacuated to remove volatile impurities. $^{13}CS_2$ (Cambridge Isotope Laboratories, 99% carbon-13) and $C^{34}S_2$ (EG&G Applied Technologies, 99% sulfur-34) samples were prepared in a similar way.

Figure 1 shows the experimental arrangement for the discharge of Ar/CS_2 mixtures using a high-frequency generator ("Tesla coil") (Model BD-20, Electro-Technic Products, Chicago, IL). Several turns of copper wire were wrapped around the quartz tube and the tip of the Tesla coil to ensure electrical contact and strengthen the discharge. Samples were passed through the discharge at 1–2 mmol/h and condensed on a CsI window held at 12 ± 1 K by an Air Products closed-cycle refrigerator. Infrared spectra were recorded at 0.5 cm^{-1} resolution in the 4000–400-cm^{-1} region using a Nicolet 7199 spectrometer with a KBr beam splitter; wavenumber accuracy is ±0.1 cm^{-1}. Selected samples were subjected to irradiation from a high-pressure mercury arc (T.J. Sales, Inc., BH-6-1, 1000 W) (broad band) or a medium-pressure mercury street light with globe removed (Philips, H39KB, 175 W) (line source) using Corning glass and water filters. Visible–ultraviolet spectra were recorded on a Cary 17 spectrometer between 1400 and 230 nm on a 12 ± 1 K sapphire window; accuracy of the measurements is approximately ±0.1 nm.

Results

Matrix spectra of discharged Ar/CS_2 samples and electronic structure calculations of product species will be described.

Infrared Spectra. An extensive series of discharge experiments was performed with Ar/CS_2 samples under a variety of experimental conditions. The major products CS and C_3S_2 were observed at 1275.4 and 1270.2 cm^{-1} and at 2078.6 and 1024.1 cm^{-1}, respectively, in all experiments. The quartz tube was discolored in the discharge experiments with a brown-black carbon–sulfur polymeric film observed by other workers.[9] After the discharge tube was thoroughly degassed and coated with the polymer film, a new photosensitive product band appeared in the deposited matrix at 1179.7 cm^{-1}. Maximizing the yield of this interesting new band was the goal of subsequent studies. A decrease of this product was noticed in subsequent experiments after air releasing the system and after cleaning the discharge tube; the product yield increased gradually from day to day if the tube was kept under vacuum and the polymer film coating was maintained.

Figure 2 shows the FTIR spectra of 4 separate Ar$^{12}CS_2$/$^{13}CS_2$ discharge experiments in the 2085–1985- and 1250–950-cm^{-1} regions featuring different isotopic enrichments. The absorptions at 2049.6 and 1997.1 cm^{-1} in the higher energy region belong to $O^{12}CS$ and $O^{13}CS$ and the lower energy portion contains an absorption at 1157.4 cm^{-1} due to S_2O,[10] which are made in the discharge by reaction with trace oxygen impurity; a small yield of CO at 2138 cm^{-1} is not shown.

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Table I. Infrared Absorptions (cm^{-1}) Observed for the ν_3 and ν_4 of Mixed ^{12}C and ^{13}C Isotopes of C_3S_2 in Solid Argon

isotopes	ν_3 (CC) antisym str	ν_4 (CS) antisym str
32-12-12-12-32 (**1**)^a	2078.6	1024.1
32-12-12-13-32 (**2**)	2063.6	1016.9
32-13-12-13-32 (**3**)	2046.5	1013.0
32-12-13-12-32 (**4**)	2032.1	1009.4
32-13-13-12-32 (**5**)	2016.4	1005.8
32-13-13-13-32 (**6**)	1998.6	998.7
34-12-12-12-32	2078.6	1019.5
34-12-12-12-34	2078.6	1014.3

^{a}Denotes label in Figure 2.

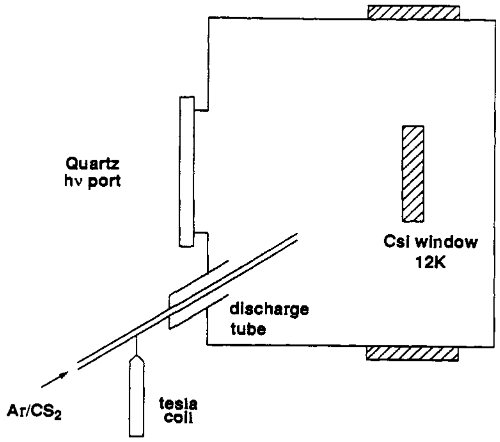

Figure 1. Schematic diagram of the apparatus used for discharge and condensation of Ar/CS$_2$ samples.

Table II. Infrared Absorptions (cm^{-1}) Observed for the ν_3 Modes of the Mixed ^{12}C, ^{13}C, ^{32}S, and ^{34}S Isotopic Molecules of C_2S_2 in Solid Argon

isotopes	ν_3 (CS) antisym str	isotopes	ν_3 (CS) antisym str
32-12-12-32 (**a**)^a	1179.7	32-12-12-34	1175.1
32-12-13-32 (**b**)	1161.9	34-12-12-34	1170.3
32-13-13-32 (**c**)	1146.4		

^{a}Denotes label in Figure 2.

Table III. Infrared Absorptions (cm^{-1}) for CS Stretching Modes for Mixed ^{12}C, ^{13}C, ^{32}S, and ^{34}S Isotopic Molecules of S(CS)$_2$ in Solid Argon

12/32	12/13/32	13/32	12/32/34	12/34
1051.1 (d)^a	1037.2 (e)	1024.3 (f)	1050.0	
			1046.0	
			1045.2	
			1041.9	1040.6
686.8	678.0	672.8	681.7	678.5

^{a}Denotes label in Figure 2.

Table IV. Carbon–Carbon Isotopic Product Absorptions (cm^{-1}) in Solid Argon for Unidentified Cumulene Type Product Species C_xS_y

12/32	mixed 12/13	13/32	12/34
1950.0	1913.6	1876.3	1948.2
(1944.7)^a		(1871.6)^a	(1943.7)^a
1877.2	1840.7, 1837.6	1802.0	1875.5
1819	1791, 1784, 1778	1748	1816

^{a}Shoulder.

Figure 2a shows a strong product absorption at 2078.6 cm^{-1} in the carbon–carbon stretching region and four bands at 1239.4 (due to ^{13}CS in natural abundance), 1179.7, 1051.1, and 1024.6 cm^{-1} in the carbon–sulfur stretching region. In addition to these product bands, weak new bands were observed at 1950, 1877, and 1819 cm^{-1}, strong ^{12}CS absorptions were observed at 1275.4 and 1270.2 cm^{-1}, and very strong undissociated CS$_2$ bands remained in the sample. With carbon-13 substitution (Figure 2d), the product bands red shifted to 1998.6, 1146.4, 1024.3, and 998.7 cm^{-1}, respectively. Parts b and c of Figure 2 show spectra with intermediate isotopic carbon enrichments. Each product absorption splits into a multiplet pattern with a ^{12,13}C mixture. Important features include two sharp triplet systems and two sharp

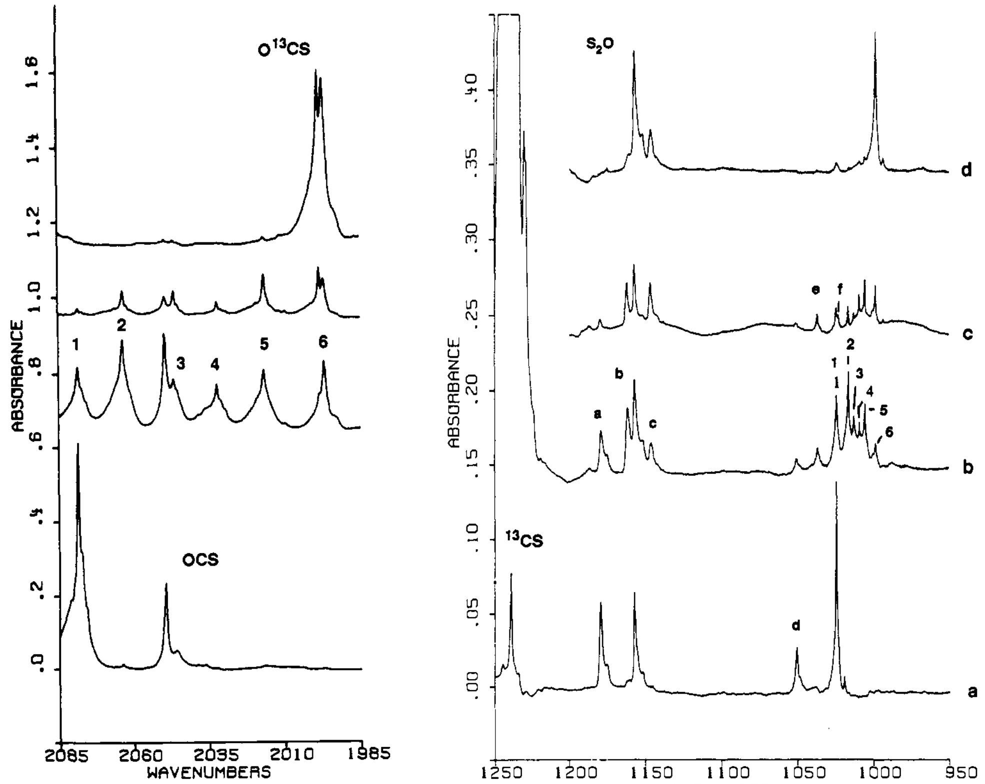

Figure 2. FTIR spectra in the 2085–1985- and 1250–950-cm^{-1} regions for Ar/CS$_2$ discharge experiments as a function of carbon-13 enrichment: (a) Ar/CS$_2$ = 100/1, (b) Ar/^{12}CS$_2$/^{13}CS$_2$ = 200/2/1, (c) Ar/^{12}CS$_2$/^{13}CS$_2$ = 200/1/2, and (d) Ar/^{13}CS$_2$ = 100/1.

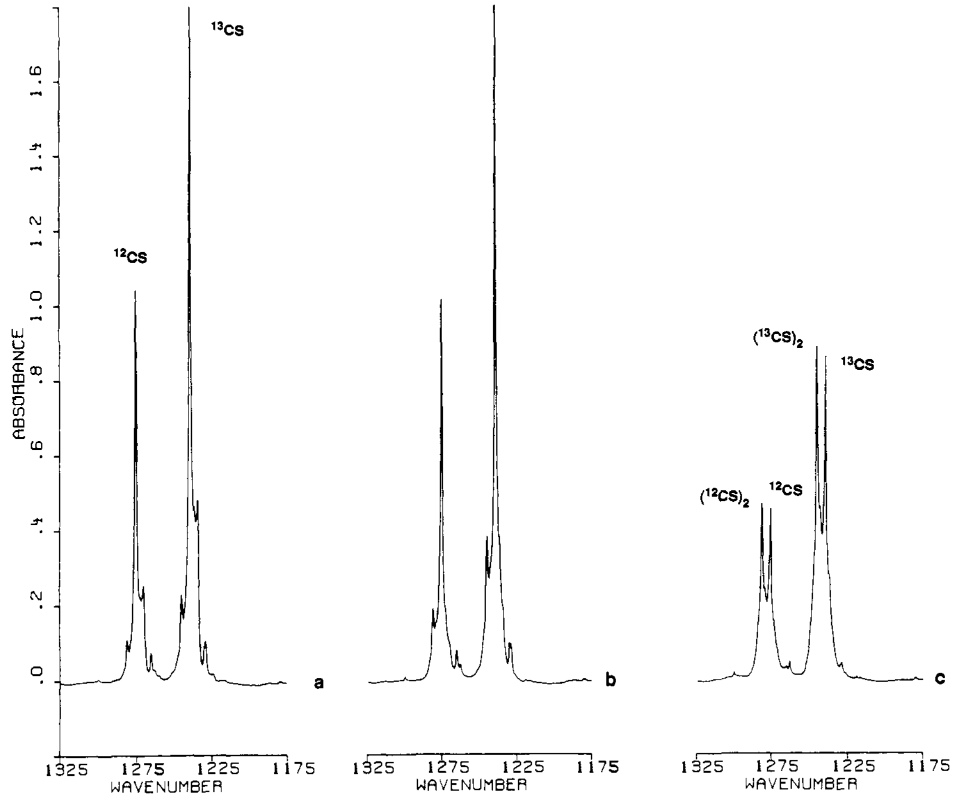

Figure 3. FTIR spectra in the 1325–1175-cm^{-1} region on contracted absorbance scale for Ar/$^{12}CS_2$/$^{13}CS_2$ = 200/1/2 sample (a) after discharge and deposition at 12 ± 1 K, (b) after annealing at 33 ± 1 K for 5 min, and (c) after annealing at 40 ± 1 K for 10 min.

sextets. The intensities of the individual components of each sextet depend on ^{13}C enrichment, and one band from each sextet tracks with one band from the other sextet (labeled 1–6). These multiplets were not observed in the spectra of isotopically pure discharged Ar/$^{12}CS_2$ or Ar/$^{13}CS_2$. Product band positions are listed in Tables I–IV.

Triplet system I (identified as **a**, **b**, **c**) has absorptions measured at 1179.7, 1161.9, and 1146.4 cm^{-} with relative intensities of 4:4:1 and 1:4:4 in Figure 2, parts b and c, respectively. The intermediate component lies 17.8 cm^{-1} lower than the ^{12}C absorption and 15.5 cm^{-1} higher than the all-^{13}C absorption, an overall $^{12-13}C$ isotopic red shift of 33.3 cm^{-1}. The absorptions were completely destroyed by high-pressure mercury arc photolysis at 320–1000 nm. A separate experiment was performed with Ar/CS_2 and the 1179.7-cm^{-1} band was observed. After the band was destroyed with 320–1000-nm radiation, photolysis using a medium-pressure mercury arc at 254 nm regenerated the 1179.7-cm^{-1} band to approximately 10% of its original intensity. Triplet system II (labeled with **d**, **e**, **f**) shows the same relative intensities as system I but different photochemistry. The intermediate component lies 13.9 cm^{-1} lower than the ^{12}C absorption and 12.9 cm^{-1} higher than the all-^{13}C absorption, an overall $^{12-13}C$ isotopic red shift of 26.8 cm^{-1}. These bands were completely destroyed by 380–1000-nm radiation. Furthermore, a low-frequency absorption at 686.8 cm^{-1} (not shown) shares similar growth and photochemical behavior with the 1051.1-cm^{-1} absorption. Discharged mixtures of $^{12}CS_2$/$^{13}CS_2$ produced new absorptions at 678.0 and 672.8 cm^{-1} in addition to the 686.8-cm^{-1} absorption.

Sample annealing to allow diffusion and reaction of trapped species was performed on several samples. A blue chemiluminescence was observed owing to the combination of S atoms to form S_2.[11,12] Annealing the sample shown in Figure 2c had little effect on the numbered and lettered product absorptions. The very strong ^{12}CS and ^{13}CS product absorptions at 1275.4 and 1239.4 cm^{-1} are shown in Figure 3a on a contracted absorbance scale and listed in Table V. Annealing at 33 K for 5 min decreased the former bands slightly while increasing bands at 1281.1 and 1245.0 cm^{-1} (Figure 3b). Further annealing at 40 K for 10 min markedly increased the latter and decreased the former bands (Figure 3c) while leaving the triplet system I bands at 1179.7, 1161.9, and 1146.4 cm^{-1} unchanged.

Table V. Infrared Absorptions (cm^{-1}) for CS and $(CS)_2$ in Solid Argon

	$^{12}C^{32}S$	$^{13}C^{32}S$	$^{12}C^{34}S$	$^{13}C^{34}S$
$(CS)_2$	1281.2	1245.1	1271.1	1234.1
CS	1275.4	1239.5	1264.9	1228.9
CS site	1270.2	1234.4	1260.0	1223.7

Discharged Ar/$C^{34}S_2$ mixtures gave prominent product absorptions (Figures 4a and 5c) at 2078.6, 1948.2, 1875.5, 1816, 1265.2, 1260.0 (not shown), 1170.3, 1040.6, and 1014.3 cm^{-1} and a weak absorption at 678.5 cm^{-1} (not shown). Photolysis of this matrix with 380–1000-nm light (Figure 4b) *decreased* the 1040.6- and 678.5-cm^{-1} absorptions by 70% and the 1170.3-cm^{-1} band by 20% and *more than doubled* the 2078.6- and 1014.3-cm^{-1} absorptions. Meanwhile, the three absorptions at 1948.2, 1875.5, and 1816 cm^{-1} decreased by 70, 90, and 80% of their original intensities, respectively. Continued photolysis (320–1000 nm) (Figure 4c) completely destroyed the 1040.6- and 678.5-cm^{-1} absorptions and decreased the 1170.3-cm^{-1} band by more than 90%. Additional growth of the 2078.6- and 1014.3-cm^{-1} $C_3{}^{34}S_2$ bands is evident.

When a Ar/$C^{32}S_2$/$C^{34}S_2$ sample was discharged, slightly different multiplet patterns were observed. The sextets from the $^{12,13}C$ (Figure 2b,c) appear as a single absorption at 2078.6 cm^{-1} and a triplet with an intermediate component at 1014.3 cm^{-1}, respectively (Figure 5b). Triplet system I showed three sharp absorptions, with an intermediate component at 1175.1 cm^{-1}. System II appears as a broadened triplet, but under closer inspection it gives rise to a higher multiplet system. The 686.8-cm^{-1} band from the $^{12}CS_2$ experiments appeared as a $^{32,34}S$ isotopic triplet at 686.8, 681.7, and 678.5 cm^{-1}.

Ultraviolet-Visible Spectra. Three experiments were performed with Ar/CS_2 samples to condition the discharge tube for maximum

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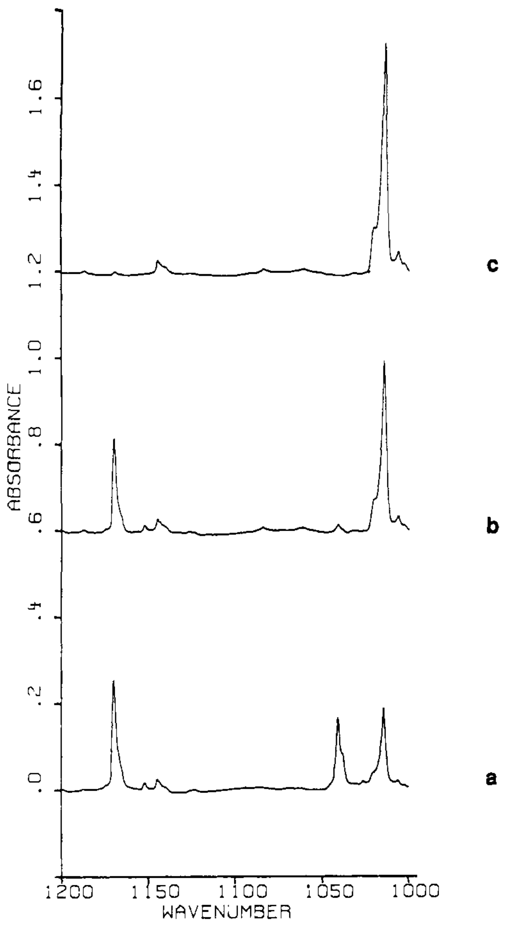

Figure 4. FTIR spectra in the 1200–1000-cm^{-1} region (a) for 13 mmol of discharged Ar/C^{34}S$_2$ = 100/1 sample deposited at 12 ± 1 K, (b) after 380–1000-nm irradiation for 30 min, and (c) after 320–1000-nm irradiation for 30 min.

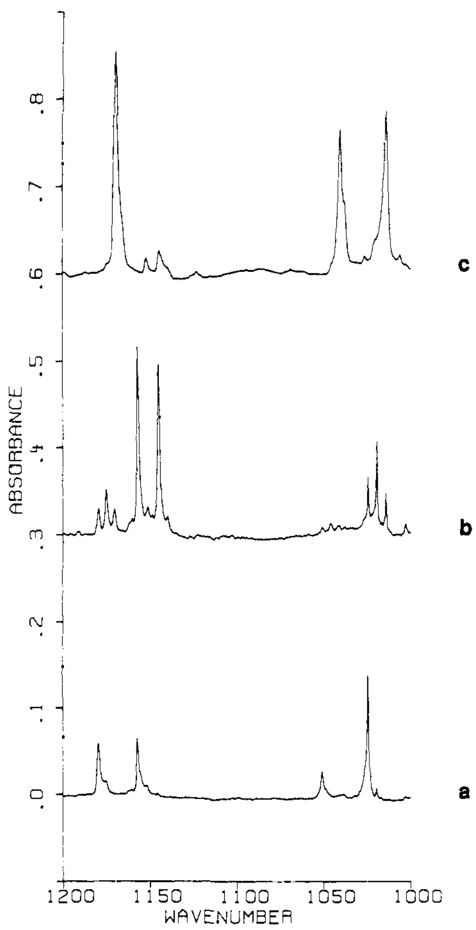

Figure 5. FTIR spectra in the 1200–1000-cm^{-1} region for Ar/CS$_2$ discharge experiments as a function of sulfur-34 enrichment: (a) Ar/C^{32}S$_2$ = 100/1, (b) Ar/C^{32}S$_2$/C^{34}S$_2$ = 200/1/1, and (c) Ar/C^{34}S$_2$ = 100/1.

Table VI. Peak Positions (cm^{-1}) in the Ultraviolet Absorption Spectra of Isotopic C$_2$S$_2$ Species[a]

peak	32-12-12-32	32-13-13-32	34-12-12-34
1	25523	25530	25523
2	25960	25954	25954
3	26055	26055	26055
4	26497	26490	26490
5	26591	26589	26596
6	27042	27034	27034
7	27152	27137	27152

[a] Frequency accuracy ±6 cm^{-1}; spacings measured between bands are accurate to better than ±6 cm^{-1}.

yield of new product species. The strongest product absorption was a sharp band at 259.8 nm with a vibronic component a 252.7 nm due to the CS diatomic,[13] and a weak vibronic band system due to S$_2$ was observed from 260 to 290 nm[14] in early experiments (Figure 6) with lower yield of the 360–390-nm vibronic system; however, S$_2$ was not observed in later experiments with the highest yield of the 360–390-nm band system. Three new absorption bands were observed in all experiments: a weak structured system in the 300–330-nm region, a strong structured vibronic system in the 360–390-nm region (Figure 7), and a weak broad band absorption from 450 to 530 nm centered at 490 nm. There was no evidence for C$_2^-$ at 520 nm, C$_2$ in the 800–1200-nm region, S$_3$ at 400 nm, nor S$_4$ at 530 or 640 nm.[13,15,16] We were unable to observe the UV absorption spectrum[17] of C$_3$S$_2$, presumably due to masking by the very strong CS absorptions. Irradiation of these matrices was performed in a like fashion to the infrared experiments, namely illumination with the broad band source was followed by irradiation with the strong line source.

Irradiation (380–1000 nm) from the broad band source completely destroyed the broad 490-nm absorption, and further irradiation (320–1000 nm) destroyed the 360–390-nm vibronic system. The strong 254-nm line source regenerated the 360–390-nm vibronic components to their original intensities. Interestingly, the strong CS band and the 300–330-nm band system were not measurably affected by photolysis.

The sharp vibronic band system in Figure 7 was scanned on expanded wavelength scale to obtain optimum resolution of vibronic structure 24 times in 6 different experiments. The peak positions were reproduced to ±0.1 nm in these experiments; the vibronic band spacings were measured directly from the chart paper and converted to cm^{-1} with an accuracy of ±6 cm^{-1}. Notice the first two vibronic intervals of 532 and 437 cm^{-1} from the data in Table VI.

The 300–330-nm-band system shows two vibronic progressions: the major progression has an average spacing of 550 cm^{-1} and asymmetry in the first two bands reveals another vibronic interval near 200 cm^{-1}.

Similar experiments were done with Ar/^{13}CS$_2$ and Ar/C^{34}S$_2$ samples, and the general features of each spectrum were the same. The vibronic spacings of the 300–330- and 360–390-nm systems showed small, reproducible isotopic shifts. Measurements for the 360–390-nm vibronic system are given in Table VI.

Calculations. Ab initio calculations have been performed on the series of cumulenes C$_n$S$_2$ (n = 1–4) as well as CS and CCS using the HONDO 7.0 program.[18] All the calculations have been

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Table VII. Ab Initio SCF/DZP Results for CS, CCS, C_nS_2 (n = 1–4) Cumulenes, and 2,3-Dithiothiirane[a]

molecule	E (S or T)	r(CS)	r(CC)	ν(CS)	ν(CC)	ν(CS) exp	ν(CC) exp
CS	−435.30694 (S)	1.5205		1426		1275.2	
CCS	−473.09388 (T)	1.5487	1.3189	942	1777		
S=C=S	−832.88224 (S)	1.5467		1583		1528.2	
S=C=C=S	−870.67438 (T)	1.5628	1.2766	1262	2112	1179.7	1904[b]
S=C=C=C=S	−908.54309 (S)	1.5497	1.2724	1081	2196	1024.1	2078.6
S=C1=C2=C3=C4=S	−946.34623 (T)	1.5581	1.2727 (1-2, 3-4)				
			1.2824	941	2007		
$S(CS)_2$	−1268.17875 (S)	1.5888	1.4283	1208	1647	1051.1	
		1.7506 (C–S′)		823		686.8	

[a] Energies in hartrees, electronic states are denoted S or T for singlets or triples, distances in Å, and frequencies in cm^{-1} (unscaled). [b] Reference 6.

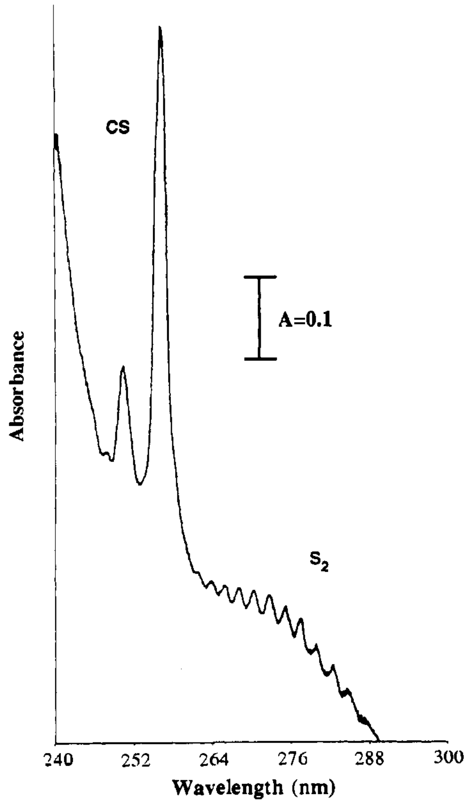

Figure 6. Representative ultraviolet absorption spectrum in the 240–300-nm region for Ar/CS_2 discharge experiments.

carried out with the restricted Hartree–Fock method and the standard double-ζ plus polarization (DZP) basis set.[19] For carbon the (9s5p) sets of Huzinaga were contracted to (3s2p) following Dunning. For sulfur, Huzinaga's (11s7p) primitive basis was contracted to (5s4p) in the manner of Dunning and Hay. A set of six d-like functions with orbital exponents α = 0.75 (carbon) and 0.6 (sulfur) was affixed to each atom, thus the complete DZP basis set has the designation C(9s5p1d/3s2p1d), S(11s7p1d/6s4p1d). Preliminary calculations were performed with the STO-3G basis set in order to locate the minima before using the larger more complete DZP basis set. Force constant calculations yielding the vibrational frequencies and IR intensities for all of the isotopically substituted molecules were also carried out in the double harmonic approximation. The calculated spectra were then compared to the experimental spectra.

The results of the ab initio calculations for the carbon sulfides are listed in Table VII; several trends are noted. The first is the alternation between singlet and triplet ground states between the series CS_2 and C_4S_2 for odd and even numbers of carbon atoms.

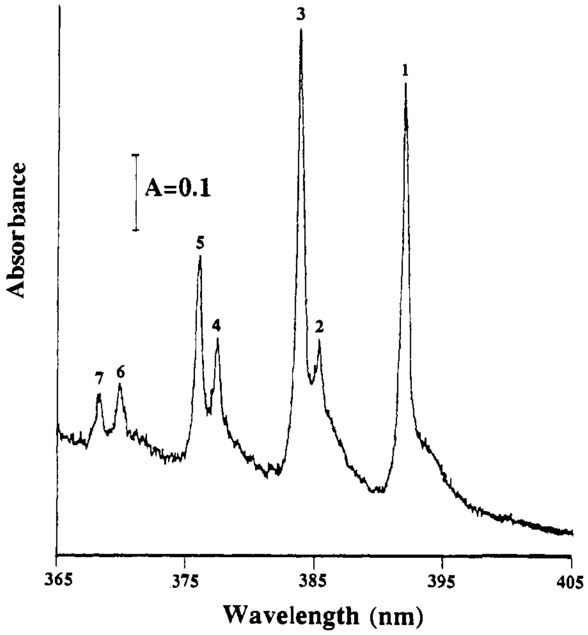

Figure 7. Vibronic absorption spectrum in the 365–405-nm region produced by condensation of discharged Ar/CS_2 mixture.

The calculated antisymmetric CS stretching mode steadily decreases with an increasing carbon atom chain length. The CS and CC bond lengths remain at 1.56 and 1.27 Å, respectively, on the average.

The structure and vibrational spectra of $S_n(CS)_2$ molecules were also investigated. Calculations predict that the $S(CS)_2$ molecule is a ground-state singlet. The bond length between the carbon atoms is 1.428 Å, which is longer than a double bond. The bond lengths for the CS groups are 1.588 Å, which is on the order of a C=S double bond. The remaining CS bond, between C and the unique S atom, is 1.7506 Å, roughly a CS single bond. Calculations predict a strong C–C mode at 1647 cm^{-1} and two strong CS vibrational modes at 1208 and 823 cm^{-1}. The latter two scale with reasonable agreement with the experimental data, and the former is probably obscured by CS_2 precursor.

Using the STO-3G minimum basis set two other molecules with C_2S_4 and C_2S_3 stoichiometries were also investigated. For the latter an alternating zigzag structure was less stable than $S(CS)_2$ while the frequencies of the former CS_2 ring dimer were too high, and even using a more extended basis set would not have matched the observed data.

Although these calculations do not include electron correlation and use moderate size basis sets, we believe that they are accurate enough to help assignment of IR absorptions. For example, Xie and Schaefer performed calculations on C_2S using different quality basis sets and configuration interaction with all single and double excitations (CISD).[20] The largest basis set used was triple-ζ with two polarization functions augmented by f-type functions. First, they show that going from SCF/DZP to CISD/TZ2P+f the

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calculated bond lengths were unchanged within 0.02 Å. Secondly, our calculated vibrational frequencies are within 3% of the CISD/TZ2P+f results. However, a reversal of the IR intensities between the CS and CC vibrations was noted when electron correlation was introduced. Therefore, the SCF/DZP calculated IR intensities are not as reliable.

Discussion

New infrared, visible, and ultraviolet absorption bands will be identified and assigned, and reaction mechanisms will be discussed. The new product bands were not present in normally deposited Ar/CS_2 samples, but they appeared when the Tesla coil discharge was sustained in the flowing gas stream. The new bands became multiplets when isotopic mixtures of $^{12,13}CS_2$ or $C^{32,34}S_2$ were discharged, which implies the presence of multiple carbon and sulfur atoms in the product molecules. Specifically, the new cumulene product molecules contain at least two equivalent carbon and sulfur atoms.

2078.6- and 1024.1-cm^{-1} absorptions: The absorptions at 2078.6 and 1024.1 cm^{-1} agree well with literature values[3,21-23] for ν_{as}(CC) and ν_{as}(CS) for C_3S_2. The six possible isotopic combinations of C_3S_2 using $^{12,13}C$ are (1) 12-12-12, (2) 12-12-13, (3) 13-12-13, (4) 12-13-12, (5) 13-13-12, (6) 13-13-13. Using the given values for the concentrations in Figure 2, parts b and c, the relative intensities are 8:8:2:4:4:1 and 1:4:4:2:8:8, respectively; the measured relative intensities for the sextet systems in Figure 2, parts b and c, agree in a qualitative sense with values calculated for the appropriate mixtures. Furthermore, the same type of sextet was observed[24] in the spectrum of mixed isotopic $^{16,18}O_3$. Therefore, the observed sextets (1–6) in the high- and low-energy regions are assigned to ν_{as}(CC) and ν_{as}(CS) stretching modes, respectively, of the different $^{12,13}C$ isotopic modifications of C_3S_2.

The isotopic combinations of C_3S_2 with $^{32,34}S$ give three possible combinations: (1) 32-12-12-12-32 (already mentioned); (2) 34-12-12-12-32; and (3) 34-12-12-12-34 (Figure 5c). The 1024.1-cm^{-1} band has already been assigned to the 32-12-12-12-32 isotope. In the Ar/$C^{34}S_2$ spectra, only one absorption at 1014.3 cm^{-1} was observed; it is identified as the 34-12-12-12-34 isomer. The mixed Ar/$C^{32,34}S_2$ sample gave the intermediate feature at 1019.5 cm^{-1}, which is assigned to the 32-12-12-12-34 isomer. The harmonic oscillator approach for calculating isotopic shifts assuming a simple C–S diatomic vibration works quite well for predicting the $^{12-13}C$ and $^{32-34}S$ red shifts. The calculated red shifts of $^{12-13}C$ and $^{32-34}S$ are 29.1 and 8.3 cm^{-1} and in close agreement with experiment.

1179.7 cm^{-1}: The 1179.7-cm^{-1} band behaves appropriately for assignment to C_2S_2. First, it is characterized by photolysis with 320–1000-nm radiation. Second, upon carbon-13 substitution, the 1179.7-cm^{-1} band becomes part of a symmetrical triplet in $^{12,13}CS_2$ experiments, which shows a varying component intensity on changing the carbon-13 enrichment. For the concentrations used in Figure 2, parts b and c, the calculated intensity ratios are 4:4:1 and 1:4:4, respectively. Again, comparison to the experimental intensities is excellent. Third, Raine et al. have predicted the antisymmetric CS stretch at 1262 cm^{-1} for the linear triplet ground-state C_2S_2 molecule.[4] Frequency calculations performed here at the DZP level also predict the fundamental at 1262 cm^{-1}. The scale factor for the Schaefer calculation was taken from CS, which is calculated 8.6% higher for the $X^1\Sigma^+$ and 6.1% higher for the $a^3\Pi$ state.[4] The average, 7.3%, predicts 1170 cm^{-1} for the antisymmetric C–S stretching mode of triplet linear C_2S_2. The present DZP calculation for C_3S_2 predicts 1082 cm^{-1} for the antisymmetric C–S mode observed here at 1024 cm^{-1}; these data define a 0.94 scale factor from C_3S_2 and predict a 1190-cm^{-1} value for C_2S_2. Both predictions from scaled ab initio calculations are in excellent agreement with the 1179.7-cm^{-1} experimental observation for C_2S_2. Therefore, the carbon isotopic triplet is assigned to the antisymmetric CS stretching mode, ν_3, for the 12-12, 12-13, and 13-13 isotopic C_2S_2 molecules. The calculated $^{12-13}C_2S_2$ red shift for the harmonic vibration of equivalent CS oscillators is 33.6 cm^{-1}, in excellent agreement with the observed 33.3-cm^{-1} shift.

The $^{32,34}S$ isotopic data also verify the identity of these absorptions as ν_{as}(CS) stretching modes of C_2S_2. The triplet structure in Figure 5b also indicates the presence of two equivalent CS oscillators. A harmonic oscillator prediction yields a 9.5-cm^{-1} $^{32-34}S$ red shift, as compared to the observed 9.4-cm^{-1} shift, thereby confirming identification as a simple CS bond stretching mode.

The present 1179.7-cm^{-1} assignment to C_2S_2 is in agreement with a 1179-cm^{-1} band recently identified as C_2S_2 on the basis of weak $^{12,13}C_2S_2$ and $C_2{}^{32,34}S_2$ mixed isotopic absorptions in natural abundance from the photolysis of bicyclic dithiocarbonate precursors[6] and the flash vacuum pyrolysis of 2,5-dithiacyclopentylideneketene.[7] The present observations for the isotopic $^{13}C_2S_2$ and $C_2{}^{34}S_2$ molecules and the symmetrical triplet mixed isotopic absorptions provide a more definitive identification of two equivalent C and S atoms and the symmetrical C_2S_2 molecule.

1051.1 and 686.8 cm^{-1}: These absorptions appear on sample deposition, photodissociate with 380–1000-nm radiation, and are not reformed by further photolysis. The 1051.1-cm^{-1} absorption becomes the highest frequency component of sharp triplet system II in the mixed $^{12,13}CS_2$ spectra (Figure 2b,c). Likewise, the 686.8-cm^{-1} band is the highest component of a triplet as well. The measured isotopic $^{12-13}C$ red shifts of 26.8 and 14.0 cm^{-1}, respectively, are near values for CS stretches when compared to the calculated 29.8- and 19.5-cm^{-1} shifts for a CS diatomic oscillator.

The $^{32,34}S$ data are very important for the identification of this molecule. Note that the triplets observed in the mixed $^{12,13}CS_2$ spectra are sharp. On the other hand, the broadening of what appeared to be a triplet results in an unresolved higher multiplet. The full $^{32-34}S$ isotopic red shift is 10.5 cm^{-1} as compared to the calculated 8.5-cm^{-1} value for a diatomic oscillator. This observation characterizes these absorptions as two equivalent CS bond stretches influenced by another unique sulfur atom. Therefore, we assign the 1051.1-cm^{-1} absorption to ν_{as} (CS) in $S(CS)_2$. The 686.8-cm^{-} band is attributed to a ring C–S stretching mode of the molecule $S(CS)_2$.

1950–1750-cm^{-1} region: The three absorptions in this region for discharged Ar/CS_2 sample have common characteristics. Most importantly, they all reveal intermediate multiplet structure using $^{12,13}CS_2$ mixtures and large $^{12,13}C$ shifts, which are appropriate for an almost pure carbon–carbon stretching mode. This shows that they belong to the stretching motions of at least two carbon atoms. Furthermore, their different photochemistry demonstrates that they belong to three distinct new carbon-containing species. Red shifts of 1–3 cm^{-1} were observed with $C^{34}S_2$ mixtures; this observation implies a small amount of coupling between the moving carbon atoms and presumably terminal sulfur atoms. Although the carbon-13 shift indicates an almost pure carbon–carbon stretching mode, the presence of still a third atom from an impurity in the discharge cannot be ruled out.

The strongest infrared band, namely the antisymmetric C=C fundamental of triplet C_4S_2, is predicted at 2007 cm^{-1} from DZP calculations. This value is clearly high by some 5–10%. The band at 1819 cm^{-1} could be due to C_4S_2. Although this band is broader and weaker than the 1950.0- and 1877.2-cm^{-1}-product bands in this region and there is some band overlap in the $^{12,13}C$ spectrum, the mixed $^{12,13}C$ observation is in accord with a C_4S_2 species. More ab initio calculations should be done on C_4S_2 including CI in order to test this possibility.

The CCS intermediate species was considered for the 1877.2-cm^{-1} band, but the present DZP and CISD(DZP) calculations[20] predict the C=C fundamental for C_2S in the 1600-100-cm^{-1} range. The sharp 1950.5- and 1877.2-cm^{-1} bands appear to be due to the vibration of two carbon atoms, but without more data, these new cumulene-type species cannot be identified.

1281.2, 1275.4, and 1270.2 cm^{-1}: The sharp 1275.4- and 1270.2-cm^{-1} bands bracket the $^{12}C^{32}S$ gas-phase 1272.2-cm^{-1} fundamental.[13] The observed 12-32/13-32 isotopic ratio (see Table V) for the 1281.2; 1275.4; and 1270.2-cm^{-1} bands, 1.0290, is just

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below the 1.0293 ratio calculated for a harmonic C–S oscillator, as expected for normal cubic contributions to anharmonicity. Likewise the 12-32/12-34 ratio, 1.00806, is slightly below the calculated harmonic value 1.00813. Figure 3 shows the dramatic increase of the 1281.2-cm^{-1} band on annealing at the expense of the 1275.4- and 1270.2-cm^{-1} bands. The latter are assigned to CS ($X^1\Sigma^+$) isolated in solid argon, and the former is identified as $(CS)_2$, the van der Waals dimer of ground-state singlet CS. The small blue shift of 5.7 cm^{-1} in the fundamental frequency from CS to $(CS)_2$ is indicative of a weak physical interaction totally unlike the chemical interaction between ^1CS and ^3CS required to form the triplet C_2S_2 molecule.

360–390 nm: The sharp vibronic system in this region (Figure 7) shows the identical photochemistry as the 1179.7-cm^{-1} C_2S_2 infrared band. The initial spacings of 532 and 437 cm^{-1} on these absorptions are appropriate for ν_2, the symmetric terminal C–S stretching mode, and ν_4, the trans bending mode, respectively, and isotopic shifts on the spacings show that both carbon and sulfur atoms are directly involved in the vibrational motions. These spacings compare favorably with scaled ab initio values for these symmetric motions not observed in the infrared spectrum.[4] The UV–vis absorption spectra of natural isotopic C_2S_2 was also measured by Maier et al.[6] and Wentrup et al.,[7] and the present spectrum is in good agreement. However, these groups were unable to resolve the second vibronic progression; higher C_2S_2 concentration and broader bands consequently decreased the resolution and accuracy of these band positions.

The strong 392-nm band system is assigned to the $A^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ absorption of C_2S_2 which is Z-dipole allowed for the linear centrosymmetric molecule. The strong vibronic progression (peaks 1, 3, 5 and 7 in Figure 7 and Table VI) in the symmetric $\nu_2(\Sigma_g^+)$ mode is fully allowed and shows intervals of 532, 541, and 556 cm^{-1}; the increase in spacing denotes quartic anharmonicity in the C–S stretching coordinate. The origin band (peak 1) has a weak, broad shoulder about 2 nm to the long wavelength side, which is probably due to interaction with another molecule in the matrix cage. The sharp, weaker band at 385.2 nm (peak 2) is, however, on top of any shoulder on the strongest vibronic band (peak 3). The further increase in intensity of sharp bands at 377.4 (peak 4) and 369.8 nm (peak 6) relative to the major vibronic progression (peaks 5 and 7) shows that the latter three sharp bands (peaks 2, 4, and 6) form a second vibronic progression in ν_1 with a similar Franck–Condon profile as the major series but displaced by one quantum. The resolved vibronic component at 385.2 nm (peak 2) is 437 cm^{-1} above the strong 391.8-nm origin of the transition. The 385.2-nm band is identified as a false origin built on one quantum of ν_4 (Π_g) in the excited state. This false vibronic origin has $\Sigma_u \times \Pi_g = \Pi_u$ symmetry and is an x, y dipole (Π_u) allowed transition. The weaker progression (peaks 2, 4, and 6) with 537- and 545-cm^{-1} intervals in ν_2 is built on this false origin.

450–530 nm: The weak broad 450–530-nm band exhibited the same photochemistry as the 1051.1- and 686.8-cm^{-1} infrared absorptions, and this absorption is tentatively assigned to $S(CS)_2$ on the basis of similar photochemistry.

300–330 nm: This weak absorption band system did not show any photochemistry. The spacings of 550 cm^{-1} with an additional progression of 200 cm^{-1} are reminiscent of symmetric (CS) stretching and bending modes for large C_xS_y species. This band is likely due to a large stable cumulene species which cannot be identified.

259.8 and 252.7 nm: The strong 259.8 nm band is red shifted 410 cm^{-1} from the gas-phase origin of the ($A^1\Pi \leftarrow X^1\Sigma^+$) transition for CS.[13] The 252.7-nm vibronic component defines a 1080 ± 10 cm^{-1} vibrational interval, slightly larger than the 1053 cm^{-1} spacing for the gaseous species. Isotopic substitution verifies the CS nature of the oscillator: the vibronic spacing is 1050 ± 10 cm^{-1} for ^{13}CS and 1066 ± 10 cm^{-1} for $C^{34}S$. The red matrix shift in the electronic origin is typical. The blue shift in the excited state vibrational spacing arises from repulsion between the matrix cage and the CS ($A^1\Pi$) vibration; recall that the strong 1275.1 cm^{-1} site of CS ($X^1\Sigma^+$) exhibited a 3.2 cm^{-1} blue vibrational matrix shift.

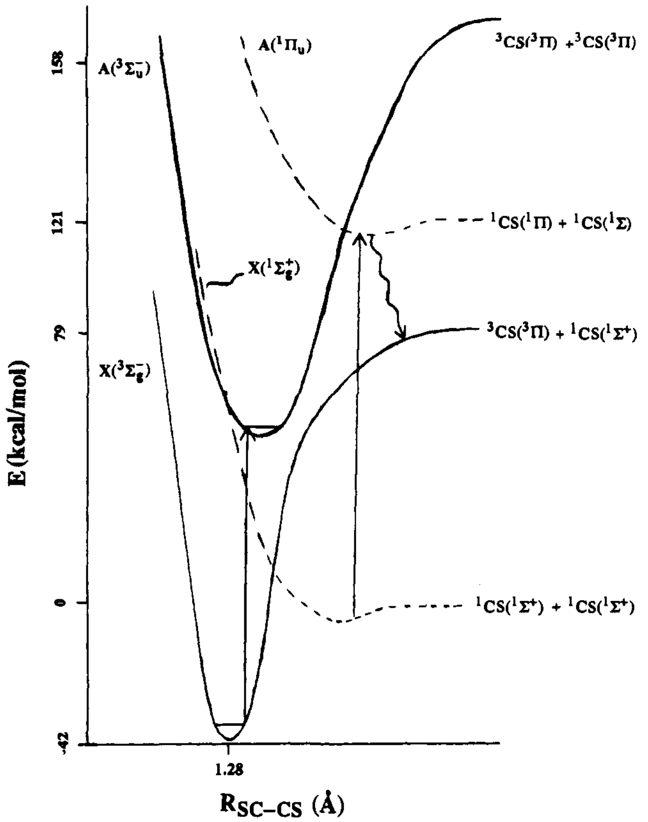

Figure 8. Schematic potential functions for triplet C_2S_2 and singlet $(CS)_2$ species.

Reaction mechanisms: In these experiments, CS_2 was dissociated by the Tesla coil discharge. Therefore, the most important reaction in the discharge tube is the production of singlet and excited triplet CS molecules:

$$CS_2 \rightarrow CS(X^1\Sigma^+) + S(^1D) \text{ and } CS\ (a^3\Pi) + S(^3P).$$

In many ways, the apparatus used to measure the $a^3\Pi$ emission spectrum of CS is similar to the discharge source of CS used here.[25] Clearly the $a^3\Pi$ state of CS is produced by the present Tesla coil discharge. Ab initio calculations have determined that the ground triplet state of C_2S_2 is stable by 121 kcal/mol with respect to dissociation into singlet and triplet CS molecules.[4] Therefore, the mechanism for triplet C_2S_2 formation in these experiments is simply the union of singlet and triplet CS molecules:

$$CS\ (X^1\Sigma^+) + CS\ (a^3\Pi) \rightarrow (X^3\Sigma_g^-)\ C_2S_2$$

This synthesis of C_2S_2 is unusual since an excited-state fragment reacts with a ground-state fragment of the same substance. The union of the two ground-state fragments produces the $(CS)_2$ van der Waals complex (1281.1-cm^{-1} absorption, Figure 3) since the singlet C_2S_2 molecule is not chemically bound. This mechanism is in accord with a theoretical prediction that the colinear reaction of ground-state CS to form C_2S_2 requires ultraviolet excitation.[26]

The C_2S_2 product formation was suppressed by oxygen. The quartz tube required through degassing and coating with carbon–sulfur polymer before the 1179.7-cm^{-1} C_2S_2 band could be observed in the matrix spectrum of the effluent gas. This observation is explained by the quenching of triplet CS by triplet O_2 and is interpreted as evidence for the requirement of triplet CS for the formation of triplet C_2S_2.

The C_2S_2 molecule photodissociated with broad-band 320–1000-nm radiation; however, photolysis with the strong 254-nm line source regenerated the C_2S_2 absorptions. The photolysis in this unique system is shown in the schematic diagram in Figure

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8, which is based on calculations[4] for C_2S_2 and diatomic molecule energies.[13] Near-ultraviolet radiation (320–400 nm) excites the allowed bound–bound $A^3\Sigma_u^- \leftarrow X^3\Sigma_g^-$ transition of C_2S_2. The excited-state $A^3\Sigma_u^-$ curve probably crosses the repulsive van der Waals $(CS)_2$ singlet curve and intersystem crossing leads to dissociation into the ground-state van der Waals dimer. Ultraviolet radiation at 254 nm is in resonance with the allowed $A^1\Pi \leftarrow X^1\Sigma^+$ transition for CS (and for the corresponding van der Waals dimers). Intersystem crossing from $A^1\Pi$(CS) to the $a^3\Pi$(CS) state of one monomer in the presence of another monomer $X^1\Sigma^+$(CS) regenerates the ground-state triplet C_2S_2 molecule. This matrix photodestruction–photosynthesis process can be recycled as long as desired.

The present reaction and photochemical regeneration mechanisms for triplet C_2S_2 formation, unfortunately, do not prove that this triplet is the ground state, but coupled with theoretical evidence that the corresponding singlet state ($^1\Sigma_g^+$) is not bound,[4] the present work provides strong evidence that the bound triplet state ($^3\Sigma_g^-$) so formed is the electronic ground state.

The remaining question, then, is whether the reaction to form C_2S_2 takes place in the discharge tube or on the surface of the condensing matrix. Singlet CS clearly survives the discharge, based on matrix observation of CS, and triplet CS also survives the discharge, based on observation of the $a^3\Pi$ emission spectrum from a similar system.[25] In fact triplet CS survives in the flow system for at least 4 ms with argon pressure in the 1-Torr range.[25] Furthermore, the radiative lifetime of $a^3\Pi$ CS has been estimated at 41 ms.[27,28] Under the pressure conditions of the present discharge tube (100–200 mTorr), triplet CS produced should live for more than 4 ms but less than 41 ms. The mass flow rate under these conditions provides a 5–10-ms time-of-flight from the discharge tube to the cold window, a period that ($a^3\Pi$) CS can clearly survive. A three-body collision is required to stabilize triplet C_2S_2 in the discharge, analogous to the formation of ozone.[24] However, unlike O_3 which is condensed intact on a 77 K wall, C_2S_2 polymerizes on the walls of the discharge tube. Therefore the yield of C_2S_2 *in the present discharge tube* is probably low. We believe that most of the triplet C_2S_2 observed here is formed by union of singlet and triplet CS on the surface of the condensing matrix where the reactive C_2S_2 species is isolated in solid argon and cannot polymerize.

Some excited C_2S_2 formed in the discharge may decompose into CCS and an S atom in the discharge:

$$(C_2S_2)^* \rightarrow CCS + S$$

Although this dissociation energy is not known, the *D*(SC–S) value of 95 kcal/mol[29] provides a reasonable model. The presence of the CCS radical in CS_2 discharges has been confirmed by observation of the CCS microwave spectrum.[1] Since there was no conclusive evidence that CCS reached the matrix, CCS was probably consumed by reactions in the discharge. Therefore, we postulate the formation of C_3S_2 through the reaction of CCS and CS in the discharge:

$$CCS + CS \rightarrow C_3S_2$$

The stable C_3S_2 molecule was also produced on photolysis of the deposited sample, which requires another mechanism. The pronounced growth of C_3S_2 on 380–1000-nm photolysis was accompanied by loss of $S(CS)_2$ and C_2S_2. A photochemical reaction of C_2S_2 and CS is suggested:

$$C_2S_2 + CS + (\lambda > 350 \text{ nm}) \rightarrow C_3S_2 + S$$

The infrared absorptions due to CS_2 were quite strong in the spectra; therefore, it is reasonable to assume that ^{3}CS can react with excess CS_2 (or that $^3CS_2$ can react with CS since there is evidence for $^3CS_2$ in discharges).[30] The mechanism proposed for $S(CS)_2$ formation is

$$a^3\Pi(CS) + CS_2 \rightarrow [^3S(CS)_2]^* \rightarrow {}^1S(CS)_2$$

Moreover, this reaction only occurs on deposition. Since annealing the matrix could not restore $S(CS)_2$ after photodissociation, one of the necessary reagents for its formation is gone. The dominant molecule with that characteristic in these experiments is ^{3}CS, which decays into the singlet ground state. Therefore, $S(CS)_2$ is probably a reaction product of ^{3}CS and CS_2.

Conclusions

Triplet CS has been generated by the Tesla coil electrical discharge of an Ar/CS_2 gas stream and used for the matrix syntheses of the transient C_2S_2 and $S(CS)_2$ molecules. The present synthesis of C_2S_2 from CS_2 is significant because of the simple reagent and mechanism for formation, which allows complete isotopic substitution for vibrational analysis and definitive identification of ethenedithione. Ab initio calculations were helpful for the assignment of ground and excited electronic state vibrational fundamentals. The production of a significant amount of ^{3}CS was very dependent on the discharge conditions. In the presence of O_2, the amount of ^{3}CS was significantly decreased by quenching, which was manifested by the decreased yield of triplet C_2S_2. This observation provides indirect evidence for the triplet ground state of C_2S_2 in agreement with the calculations of Schaefer et al.[4]

Since CS is known to exist in the interstellar medium,[31,32] the carbon sulfides produced in these experiments may also exist in the interstellar medium and in cometary ices, which are rich in carbon and sulfur. It is feasible for ^{3}CS to be produced on or near the surfaces of cometary ices, by absorptions of near-ultraviolet radiation, and to react as observed in the present matrix isolation study.

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Registry No. CS, 2944-05-0; C_3S_2, 627-34-9; C_2S_2, 83917-77-5; ^{13}C, 14762-74-4; ^{34}S, 13965-97-4; CS_2, 75-15-0; C_2S, 12602-41-4; C_4S_2, 122293-58-7; C_2S_3, 141784-27-2.

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