# Infrared identification of the FCS radical in an argon matrix

Nico Caspary, Brent E. Wurfel, Anton Thoma, Günter Schallmoser and Vladimir E. Bondybey Institut für Physikalische und Theoretische Chemie der Technischen Universität München, D-85747 Garching, Germany

Received 14 May 1993

The FCS radical has been produced using a pulsed-jet DC discharge technique with several precursor molecules and characterized by IR absorption spectroscopy in an argon matrix. The spectra were analyzed and the following vibrational assignments, confirmed by isotopic studies, and by normal coordinate analysis were determined:  $v_1 = 1297.9 \text{ cm}^{-1}$ ,  $2v_2 = 910.3 \text{ cm}^{-1}$  in Fermi resonance with  $v_3 = 917.9 \text{ cm}^{-1}$ , and  $v_1 + v_3 = 2202.6 \text{ cm}^{-1}$  in Fermi resonance with  $2v_2 + v_3 = 2195.7 \text{ cm}^{-1}$ .

# 1. Introduction

Formyl, fluoroformyl and chloroformyl radicals have been the subjects of several spectroscopic investigations in the past decades and are well characterized [1]. In contrast to these molecules the knowledge of the corresponding sulfur containing molecules is quite limited. Several theoretical studies have predicted the structure and spectroscopic constants of HCS [2,3], FCS [4,5] and CICS [5]. While the theoretical investigations on FCS were motivated by the experimental observation of a chemiluminescence spectrum, which had been assigned to FCS [6,7], later isotopic studies have shown that the molecule could not contain carbon and caused the authors to withdraw his assignment [8].

Recently our group has produced ClCS in a pulsedjet DC discharge and characterized it by its infrared absorption in an argon matrix [9]. This pulsed discharge technique could be used to produce ClCS and many other radicals by the fragmentation and reactions of precursor gases [10]. The same technique was used here in a series of experiments directed towards the production and spectroscopic characterization of FCS in solid argon. The molecule was generated by the reaction of the CS<sub>2</sub> fragment, CS with a fluorine atom provided by  $C_2F_4$ ,  $SF_6$ , or the teflon of the discharge channel or other reaction pathways using these precursors. Using a Fourier transform spectrometer, we identified all three ground state fundamental frequencies of FCS isolated in an argon matrix. The vibrational assignments were confirmed by isotopic substitution experiments and by normal coordinate analysis. The assignments were also aided by the observation of photodecomposition of FCS into F+CS by blue laser light near 440 nm. A comparison of our results with theoretical predictions is given.

#### 2. Experimental

The description of our experimental apparatus has been given previously [10]; here we give only a brief outline and details pertaining to this investigation. The exit of the pulsed discharge source has been placed 25 mm from a cooled KCl window. Later spectra, after the APD Cryogenics HC-2D closed cycle refrigerator used in these studies was returned from maintainance, were recorded at 11-13 K. Earlier experiments have been performed with KCl window temperatures of 16-18 K. Argon, 99.999%, and  $SF_6$ , 99.9%, were obtained from Messer Griesheim. CS<sub>2</sub>, 99%, was acquired from Merck Schuchardt.  $C_2F_4$ , stated to be greater than 97% pure was purchased from PCR Inc. <sup>13</sup>CS<sub>2</sub>, <sup>13</sup>C 99%, was obtained from Cambridge Isotope Laboratories. The SF<sub>6</sub> and CS<sub>2</sub> were purified by several trap to trap distillations. The <sup>13</sup>CS<sub>2</sub> was degassed before use.

The gas mixtures were made by standard procedures and stored in glass bulbs. Normally 3-4 mmol were deposited at a 1 mmol per hour rate. The pulsed valve was operated at 2.5 Hz with a 1-3 ms opening time. The discharge voltages were in the range of 500 to 1200 V with approximately  $(0.5-5) \times 10^{-6}$  C per pulse. After deposition infrared, near-infrared, visible and near-ultraviolet spectra were taken at 0.06, 0.5, 1.0 and 1.0 cm<sup>-1</sup> resolution, respectively, with a Bruker IFS 120 HR Fourier transform spectrometer. Laser-induced fluorescence spectra were also recorded using a cw argon ion laser pumped dye laser (stilbene 3 and rhodamine 6G). The Fourier transform spectrometer was also used to collect the fluorescence at 1.0 cm<sup>-1</sup> resolution.

## 3. Results

To generate FCS, mixtures of  $CS_2/SF_6/Ar$  and  $CS_2/C_2F_4/Ar$  have been discharged. FCS was expected to be formed by reactions in the discharge, or during deposition on the KCl window. To identify the FCS absorptions, and rule out those species which do not contain all three elements, several control experiments were carried out, in which  $CS_2/Ar$ ,  $SF_6/Ar$ , or  $C_2F_4/Ar$  alone have been discharged.

Although SF<sub>6</sub> is known to quench discharges and is therefore used as a protective gas, a stable discharge could be maintained at 500 V with a concentration of 1/600 in argon. The IR spectrum of this matrix showed absorptions of the fragments SF<sub>3</sub>, SF<sub>4</sub>, SF<sub>5</sub> and a large parent peak extending from 900 to 965 cm<sup>-1</sup>. The IR spectra of matrices produced by discharging  $C_2F_4/Ar$  samples have previously been described [11]. Besides the parent peaks, the main products are CF, CF<sub>2</sub>, CF<sub>3</sub>, CF<sub>4</sub>, C<sub>2</sub>F<sub>3</sub> and C<sub>2</sub>F<sub>6</sub>.

Several experiments with  $CS_2/Ar$  mixtures (1/ 400) were also performed. A section of a spectrum obtained with a discharge voltage of 600 V is shown in fig. 1a. In this spectrum CS, SCCCS, and SCCS were the major products, as identified by their infrared absorptions. In a spectrum produced by a "harder" discharge at 1200 V, a part of which is shown in fig. 1b, numerous additional absorptions were observed. In the infrared, fluorine-containing species such as  $CF_2$ , SF, and  $F_2CS$  were identified. AlC was detected by visible absorption and laser-induced fluorescence [12]. Clearly the higher discharge voltage leads to some amount of reactive sputtering of the surfaces of the aluminum electrodes



Fig. 1. Infrared spectra,  $1200-1400 \text{ cm}^{-1}$  of Ar matrices made with a pulsed-jet discharge technique, using the following mixtures and discharge voltages: (a) CS<sub>2</sub>/Ar, 1:400, 500 V, (b) CS<sub>2</sub>/ Ar, 1:400, 1200 V, (c) CS<sub>2</sub>/SF<sub>6</sub>/Ar, 1:1:400, 800 V, (d) CS<sub>2</sub>/ C<sub>2</sub>F<sub>4</sub>/Ar, 1:1:400, 800 V. In (a) and (b) parts of the spectra are expanded by a factor of 5 along the y axes. The arrows point out the good correlation of the FCS absorption at 1297.4 cm<sup>-1</sup> and the F<sub>2</sub>CS absorption at 1353.3 cm<sup>-1</sup>. Table 1 gives a listing of frequencies, intensities and assignments in the region from 600 to 1500 cm<sup>-1</sup> of the spectra partially shown in b, c and d.

and of the teflon discharge channel. In the same experiment new unknown peaks at 1297.4, 910.3, and 917.9 cm<sup>-1</sup> were detected (table 1).

Fig. 1c shows the relevant section of a spectrum obtained by discharging a  $SF_6/CS_2/Ar$  mixture (800 V). Along with products already listed above, infrared absorptions of  $SF_2$  and  $SSF_2$  could also be identified (table 1). The region from 900 to 965 cm<sup>-1</sup> was obscured by the extremely intense  $SF_6$  parent peak, while the unknown absorption at 1297.4 cm<sup>-1</sup> reported above was also present with appreciable intensity.

To avoid the problem of  $SF_6$  interference,  $C_2F_4$  was used as a fluorine source in several experiments. In

#### Table 1

Frequencies and approximate intensities of molecular species which appear between 600 and 1500 cm<sup>-1</sup> after discharge of the following mixtures:  $CS_2/SF_6/Ar$  (800 V),  $CS_2/C_2F_4/Ar$  (800 V),  $CS_2/Ar$  (1200 V)

Frequency (cm <sup>-1</sup> ), intensity *)				Assignment			
CS <sub>2</sub> +	CS <sub>2</sub> +	CS <sub>2</sub> +	lit.	molecule	mode	ref.	
SF <sub>6</sub>	C <sub>2</sub> F <sub>4</sub> <sup>b)</sup>	teflon, Al <sup>c)</sup>	value				
	610.6 vw						
611.9 s			613.1	SF <sub>6</sub>	V4	[13,14]	
620-710 вв				SF₄			
620.9 vw	620.6 vw		621	F <sub>2</sub> CS	V <sub>6</sub>	[15]	
633.6 w	633.7 w		631	CF4		[16]	
	667.6 w		668.0	CF,	¥7	[11,16]	
668.2 w				-	-	• / -	
	675.7 w	675.7 vw					
679.3 w							
		680.0 vw					
682.3 s	682.1 w		682.3	SF <sub>3</sub>	asym.ax.S-F	[17]	
				-	stretch		
688.4 w			688.7	$(SF_4)_2$		[14]	
	696.6 w	696.6 w					
	703.3 m		703.2	CF3	V2	[11,16]	
706.0 s, 708.8 s	705.2 w,		704.3-	SF₄	V <sub>6</sub>	[16-19]	
+ sites	708.6 vw		708.7				
710.0 w			713.8 <sup>d)</sup>	SSF₂	V2	[20]	
	714.0 vw		715	$C_2F_6$		[16]	
716 760 14				SSE			
/13=/00.00				3312			
		737 0 101					
757 A m	752 2 VW	157.0 **	758 d)	SSF.	И.	[20]	
752. <b>4</b> III	752.2 44	771 8 vw	150	551 2	*1	[20]	
		171.0 ***					
775-828 bb				SF <sub>2</sub> ,			
				SF5, SF			
777.8 w	777.6 w						
	787.9 w		787.2	F <sub>2</sub> CS	V <sub>2</sub>	[15]	
804.4 m-s	804.8 w		804.6	SF <sub>2</sub>	V <sub>3</sub>	[17,21]	
812.2 m			813.1, 811.8	SF₅	asym.S-F	[13,17]	
					stretch		
821.8 m	822.1 m	822.2 w	822	SF		[17]	
832.2 m	832.5 w		832.5	SF <sub>2</sub>	ν <sub>l</sub>	[17,21]	
837-867 bb				SF.			
844 0 m	843 8 vw		843.8	SF <sub>2</sub>	sym.eg.S-F	[17]	
• /T/U III	012.01.0		51010	3	stretch	·J	
848 8 w				SF <sub>2</sub> site	21		
0.0.0 4		852.4 w					
856.5 s.			856.4,	SF₄	ν <sub>R</sub>	[16-19]	
859.2 s			859.7	-	-		
	857.1 vw	857.1 w					

Table 1
Continued

Frequency (cm <sup>-1</sup> ), i	intensity *)			Assignment		
CS <sub>2</sub> + SF <sub>6</sub>	$CS_2 + C_2F_4^{b}$	CS <sub>2</sub> + teflon, Al °)	lit. value	molecule	mode	ref.
867-895 bb				SF4		
869 0 w				SF4	$v_s + v_c$	[22]
884.6 s	884.5 vw		884.5	SF₄	$\nu_1$	[16-19]
	887 6 vw	887 6 vw				
	900.0 vw	007.074	900	C.F.	V.	[11]
	903.0 vw	903.0 vw	,	024 3	~ 4	[]
905-950 vs			921.2, 927.7	SF6	V <sub>3</sub>	[13,14,22]
	010.4 m	010 2 100	938.0, 943.0	FCS	7	
	910.4 W 916 9 w	310'3 AM		rus C.F.	4 <b>v</b> 2	
	910.8 w	0170 vvv		C21 4 FCS	V.	
	921.0 w	71/.7 ¥ W		CaE	× 3	
	221.V W	928.1 vw		- <u>2</u> + 4		
	931.7 vw	931.7 w				
		943.9 vw				
988.8			989.0	SF <sub>6</sub>	$v_2 + v_6$	[22]
	1 <b>019.6 vw</b>	1019.5 vw				-
	1024.7 w-m	1024.7 m		$C_3S_2$	V4	[23,24]
	1025.3 w					
	1028.7 vw		- · · · · · · · · · · · · · · · · · · ·			
	1033.5/1034.9 s		1034.9, 1038 <sup>e)</sup>			[11,16]
	1038.7 vw					
	1042.4 w					
	1040.4 vw	1074 2	1074 1	1305		[11 16]
1080 8 171	10/ <b>4.</b> 2 m	1074.3 vw	10/4.1	CF2	$\nu_3$	[11,10]
1086 3 vw	1086 4 s-m		1086.4	CE	ν.	[11 16]
1102.0 w	1000.4 s=m	1102.2 w	1102.1	CF <sub>2</sub>	V1 V2	[11,10]
1102.0 %	1111.1 m	1102.2 0	1111.2		• 3	[11,16]
1127.1 w				0200		[,.]
	1133.0 w					
1140.0 m	11 <b>40.0 w</b>					
1160.5 vw	1160.5 w					
1164.7 vw				13		
	1164.9 vs			<sup>13</sup> CCF <sub>4</sub>		
	1171.3 m		1173 *			[16]
	1175-1182					
	1178.5 vs			$C_2F_4$		
1180.0 w		1180.2 w	1179.9	SCCS	V3	[23]
1187.4 w					· .	L-~1
	1193.7 w					
1212.4 w	1212.4 m	1212.4 vw	1212	F <sub>2</sub> CS	$v_2 + v_5$	[15]
	121 <b>4</b> .1 vw					
1215.0 vw	1215.1 vw			~ -		
	1216.9 m	1000 0	1216.9	$C_2F_3$	ν <sub>3</sub>	[11]
	1220.6 \$	1220 <b>.9</b> vw	1220.5	CF <sub>2</sub>	ν <sub>3</sub>	[11,16]
1222.0	122 <b>4./ vw</b>	1224 2				
14JJ.7 W	1234,UW 1230 3 m ch	1234.2 VW	1210 2	1308		[10]
	1237.3 W 311	1237.3 W	1437.4	C.3		[+v]

Table	1
Contir	ued

Frequency (cm <sup>-1</sup> ), intensity <sup>a)</sup>				Assignment	nent		
CS <sub>2</sub> + SF <sub>6</sub>	$\begin{array}{c} CS_2 + \\ C_2F_4 \end{array}$	CS <sub>2</sub> + teflon, Al <sup>c)</sup>	lit. value	molecule	mode	ref.	
	1240–1243 m-w			many peaks sites of			
	1243.7 m		1243.8	$C_2 F_6$		[11,16]	
1250.3 m-w	1250.4 vs	1251.3 vw	1250.5	CF <sub>3</sub>	V <sub>3</sub>	[11,16]	
	1253.7 vw						
1256.8 w	1256.8 m						
	1258.2 vw	12.58.5 w					
1263.2 m-w	1263.3 w	1263.3 w		(CS)X? <sup>f</sup> )			
	1265.1 w	1265.0 m	1264.9	C <sup>34</sup> S		[10]	
	1269.9 m-w	1270.0 s					
1270-1273 sh m-s							
1274.2 s	1274.3 vs		1274.2	CF₄		[11,16]	
1275.2 w sh	1275.1 vs	1275.2 vs	1275.1	CS		[10]	
	1277.1 m		1277.2	CF		[11,25]	
	1281.0 vw	1281.3 w		(CS) <sub>2</sub>		[23]	
	1282.4 m		1282.4	$C_2F_3$	v <sub>2</sub>	[11]	
	1 <b>286</b> .7 vw						
1288.7 vw	1288.8 vw	1288.7 w					
	1294.4 w-vw			FC <sup>34</sup> S	ν <sub>1</sub>		
1297.4 m	1297.4 vs 1305.7	1297.4 w		FCS	V <sub>1</sub>		
1309.7 w	1309.9 m	1310.0 vw 1322.8 vw	1310	F <sub>2</sub> CS	$\nu_2 + \nu_3$	[15]	
	1327.2 vs			$C_2F_4$			
1340.5 vw	1340.6 m		1340.6	FCCF	V3	[11]	
1349.9 vw	1 <b>349.8 w</b>			F <sub>2</sub> C <sup>34</sup> S? <sup>8)</sup>	-		
1253-1256	1253-1256			sites of			
1353.3 s	1353.3 vs	1353.3 m	1354	F <sub>2</sub> CS	$\nu_1$	[15]	
1354.6 s	1354.5 vs	1354.4 w		site			
1430.7 m	1430.7 w	1430.6 vw					
-1436							
1478.4 vs	1478.4 vs	1478.4 vs		<sup>13</sup> CS <sub>2</sub>	ν <sub>3</sub>	[9]	

a) vw=very weak, w=weak, m=medium, s=strong, vs=very strong, bb=broad band.

<sup>b)</sup> Peaks that have been observed in a spectrum of a discharge with only C<sub>2</sub>F<sub>4</sub> as precursor and could not be identified are neglected.

c) The high discharge voltage of 1200 V supports sputtering of material from the aluminum electrodes and the teflon discharge channel.

d) Neon matrix data.

e) A similar absorption was described in the given reference, but not assigned.

<sup>(1)</sup> Upon annealing a strong increase of this absorption could be observed in very good correlation with the decrease of the CS absorption at 1275.1 cm<sup>-1</sup>.

<sup>8)</sup> In ref. [15] a calculated red-shift of 2.4 cm<sup>-1</sup> for  $F_2C^{34}S$  was given, but a corresponding absorption was not reported.

a typical discharge experiment with  $C_2F_4/CS_2/Ar$  at 800 V the same absorbers were produced as with each of the precursors alone. In the spectrum, shown in part in fig. 1d, one could, in addition, observe the

absorption bands of  $F_2CS$ , as well as of several unknown species. Among those, the strong absorption at 1297.4 cm<sup>-1</sup> as well as the weaker peaks at 910.3 and 917.9 cm<sup>-1</sup> were present again. The intensity of the new absorption at 1297.4  $\text{cm}^{-1}$  correlates well with the intensity of the F<sub>2</sub>CS absorption at 1353.3  $\text{cm}^{-1}$ , throughout figs. 1a-1d.

To assist further with the assignment of the individual absorptions, several isotopic experiments with  $^{13}CS_2$  were performed. After the discharge of a  $^{13}CS_2/$  $SF_6/Ar$  sample, a new absorption appeared at 1259.3 cm<sup>-1</sup>, 38.1 cm<sup>-1</sup> from the peak at 1297.9 cm<sup>-1</sup>, observed in the experiments with carbon in its natural abundance. Since the <sup>13</sup>C shifts of CS (table 1) and CF [25] are 35.9 and 30 cm<sup>-1</sup>, respectively, and the <sup>13</sup>C shift of  $\nu_1$  of F<sub>2</sub>CS has been calculated to be 43.6  $cm^{-1}$  [15], this peak is in the region where a  ${}^{13}C$ shifted counterpart of an FCS band at 1297.4 cm<sup>-1</sup> would be expected. It should be noted that in this sample a band at 1297.2 cm<sup>-1</sup> was also observed very close to the 1297.4 cm<sup>-1</sup> absorption in the <sup>12</sup>C experiment mentioned above. This band can, however, be assigned to  $F_2^{13}CS$ . According to Haas et al. [15] a strong Fermi resonance between  $v_1$  and  $v_2 + v_3$  takes place in this molecule. The  $F_2^{12}CS v_1$  mode at 1354  $cm^{-1}$  appears as a doublet of similarly shaped bands at 1322.8 and 1297.2 cm<sup>-1</sup>, respectively. Also the peaks at 910.3 and 917.9  $\text{cm}^{-1}$  shift upon <sup>13</sup>C isotopic substitution, and new peaks at 895.3 and 904.6  $cm^{-1}$  appear. The latter absorptions could be found, although they were weak, in the spectra of the  ${}^{13}CS_2/$ SF<sub>6</sub>/Ar matrix, too.

Absorptions belonging to the same carrier molecule usually exhibit (with some exceptions) in different samples similar relative intensities. Constancy in relative intensities in samples subjected to varying treatment or obtained under different experimental conditions can therefore be useful in identifying bands due to the same absorber. One way to change these conditions is to induce chemical reactions in the matrix by annealing or photolysis. Irradiation of the matrix samples by the light of a tungsten lamp or by laser light (e.g. during a laser-induced fluorescence experiment) can often induce chemical reactions. Taking the infrared absorption spectrum before and after such irradiation, and observing the induced spectral changes can therefore be instructive. Modern FT instruments, with digital acquisition of the spectra, permit easy spectral subtraction, and allow very sensitive detection of even minor changes in the spectrum.

This can be exemplified by a series of experiments

in which we observed changes in the IR spectra of a matrix produced by the discharge of a  ${}^{13}CS_2/C_2F_4/$ Ar sample. The sample contained comparable concentrations of <sup>13</sup>C and <sup>12</sup>C. In fig. 2a we observe that after periods of irradiation with light of a stilbene 3 dye laser near 440 nm there is a rather strong decrease in the IR absorptions discussed above at 1297.4, 917.9 and 910.3 cm<sup>-1</sup>, as well as of their <sup>13</sup>C counterparts at 1259.3, 904.6 and 895.3  $\text{cm}^{-1}$ . They all appear in the difference spectrum as strong, negative going peaks. Other numerous peaks, in some cases much stronger absorptions in this spectral region, due to species not affected by the photolysis, cancel out in the subtraction process and do not appear in the difference spectrum. Some stronger bands can be seen in the spectrum as "derivative" shapes. This is due to slight spectral shifts of the respective absorptions owing to the annealing effect of the photolytic irradiation.

The high sensitivity for detecting minor spectral changes in the difference spectra permitted the identification of similar overtone or combination bands at 2143.7, 2151.1, 2195.7, and 2202.6 cm<sup>-1</sup> (fig. 2). Weak red-shifted satellites of the peaks at 1297.4 and 1259.3 cm<sup>-1</sup> appearing at 1294.3 and 1256.2 cm<sup>-1</sup>, respectively, which were scarcely detectable in the simple absorption spectra are also clearly visible in the difference traces.

The effects of photolysis can often be reversed by annealing of the sample. This permits diffusion and recombination of the fragments, and reappearance of the photolyzed species. This is demonstrated in fig. 2b, resulting from annealing the matrix from fig. 2a to 34 K. While most of the absorption bands show a small loss of intensity, perhaps due to slight aggregation reactions, or cracking of the matrix, the new absorptions mentioned above all exhibit a considerable increase in intensity.

# 4. Discussion

The above discussed data show clearly that the IR absorptions at 1297.4 (1294.3), 917.9 and 910.3 cm<sup>-1</sup>, the weak overtones at 2202.6 and 2195.7 cm<sup>-1</sup>, as well as the corresponding <sup>13</sup>C bands at 1259.3 (1256.2), 904.6, 895.3, 2151.1 and 2143.7 cm<sup>-1</sup>, show a behavior that is unique among all the



Fig. 2. Spectra obtained by spectral subtraction of IR spectra of an argon matrix, containing  $F^{12}CS$  (peaks marked with an asterisk) and  $F^{13}CS$  (labelled with +). The sample was produced by a discharge (1200 V) of a  ${}^{13}CS_2/C_2F_4/Ar$  (1:1:400) mixture. An expansion of the spectra along the y axis by a factor of 10, respectively, to the region from 1000 to 1400 cm<sup>-1</sup> has been performed between 600 and 1000 cm<sup>-1</sup>, and by a factor of 50 around 2200 cm<sup>-1</sup>. (a) Depicts the absolute change of absorption after photolysis, obtained by subtracting a spectrum recorded before irradiation with laser light ( $\lambda$  near 440 nm) from the spectrum of the same matrix scanned after irradiation. The difference spectrum shown in (b) demonstrates the change in absorption induced by annealing the photolyzed matrix to 34 K. The frequencies assigned to the isotopomers of FCS are listed in table 2.

absorptions observed over the whole IR region from 500 to 4000 cm<sup>-1</sup>. They are all photolyzed by blue light, and recover their intensities upon annealing. In view of this constancy of relative intensities and parallel behaviour, we conclude that these peaks belong to isotopomers of the same molecule.

Based on the numerous experiments with different precursors, it is evident, that the molecule must contain carbon, sulphur and fluorine. Its absorptions appear reproducibly when all three elements are present, and are not present when one of them is missing. They are absent when  $CS_2$  alone is discharged "softly" at 500 V and there is no detectable incidence of sputtered fluorine in the matrix, when only  $SF_6$  is discharged and carbon is missing, or when  $C_2F_4$ alone is used and no sulphur is present. According to fig. 1 there is a good correlation of the strongest absorption of this molecule to an absorption of  $F_2CS$ , which is the only known molecule in our spectra containing F, C, and S atoms. We therefore conclude that the molecules has a general formula  $F_xC_yS_z$ .

The fact that there is only one <sup>13</sup>C shifted peak for each <sup>12</sup>C peak indicates that this molecule contains only one carbon atom, that is y=1. In the difference spectra, displaying the change of IR absorbance, satellite peaks at 1256.2 and 1294.3 cm<sup>-1</sup> are clearly observed. Their red-shift as well as their relative intensity of  $5\pm2$  percent to the strong absorptions at 1297.9 (1259.3) cm<sup>-1</sup> suggests that they are <sup>34</sup>S isotopic peaks of a molecule containing one sulfur atom (natural abundance of sulfur isotopes: <sup>32</sup>S: 95%, <sup>33</sup>S; 0.8%, <sup>34</sup>S: 4.2%), and z=1 in the above formula. Regarding the value of x, it cannot be 2 since  $F_2CS$  is already known [15] and is also identified in our matrices. An  $F_3CS$  molecule, or any molecule with a still larger value of x would be expected to show more than one infrared active CF vibration in the region between 1300 and 1000 cm<sup>-1</sup> [26]. Furthermore, the fluorine source of the CS<sub>2</sub>/Ar "hard" discharge, the teflon of the discharge channel, did not provide enough fluorine for the production of a detectable amount of any molecule, containing more than two fluorine atoms such as CF<sub>3</sub>. The fact that the new molecule has been observed in this experiment also gives rise to x < 3. We therefore conclude that x=1also, and assign the absorber to FCS.

The photochemistry that aids us in the identification of FCS is similar to that of FCO [27]. Subjecting argon matrices containing FCO to radiation of wavelengths shorter than 280 nm also results in the decrease of FCO absorptions. This was attributed to photodecomposition of FCO into F+CO. Since in the present work we could not observe, after irradiation, the appearance of any new absorptions which could be indicative of an isomerization process, but only a slight increase in CS peak, we assume that the photolysis FCS +  $h\nu \rightarrow$  F + CS takes place. The fluorine atom can apparently diffuse in an argon matrix [28] sufficiently far to prevent immediate geminant recombination of all molecules. If the matrix is subsequently annealed, the diffusion of fluorine atoms is enhanced, and a partial recovery of the FCS absorptions due to recombination is observed.

The ab initio calculation of Chan and Goddard [5], who predicted FCS vibrations  $v_1$ ,  $v_2$  and  $v_3$  to be 1429 cm<sup>-1</sup>, 486 cm<sup>-1</sup>, and 1013 cm<sup>-1</sup>, respectively, may provide a first clue to the assignment.

From comparisons of the frequencies given in the same Letter for CICS with the experimental values [9], we expect them to be overestimated. Table 2 compares the RCISD predicted harmonic frequencies, which are considered to be the most reliable ones [5], with our assignments.

An assignment of the intense  $1297.4 \text{ cm}^{-1}$  band to  $\nu_1$  of FCS, and of the 1259.3 cm<sup>-1</sup> absorption to its <sup>13</sup>C counterpart seems obvious. In the region near  $900 \text{ cm}^{-1}$  one fundamental vibration is expected, but two bands are observed. One can note a difference between the F<sup>12</sup>CS and the F<sup>13</sup>CS isotopic molecules; the ratio of absorbances from the peak at 917.9  $cm^{-1}$  to that at 910.3 cm<sup>-1</sup>, measured by integrating the peaks in a difference spectrum, is about 1:0.82. On the other hand, the ratio of the absorbances of 904.6 to 895.3 cm<sup>-1</sup> in the <sup>13</sup>C experiment (which might be expected to have about the same value) is 0.39:1. This and the fact that the pairs of peaks are so close together suggests that each pair consists of two vibrations being in isotopically dependent Fermi resonance. We therefore assign the more intensive bands of each doublet, at 917.9 cm<sup>-1</sup> and at 895.3  $cm^{-1}$  to  $\nu_3$ , of F<sup>12</sup>CS and F<sup>13</sup>CS, respectively. They are in isotopic dependent Fermi resonance with the overtones of the bend  $2\nu_2$ , which exhibits absorptions at 910.3 and 904.6  $cm^{-1}$ . Finally, the weak bands observed at 2202.6 and 2195.7  $cm^{-1}$  (and their <sup>13</sup>C isotopic counterparts 2151.1 and 2143.7  $cm^{-1}$ ) are assigned to combination bands involving the Fermi resonance levels at 917.9 and 910.3 cm<sup>-1</sup> and  $\nu_1$ , that is to  $\nu_1 + \nu_3$  and  $\nu_1 + 2\nu_2$ . Table 2 gives a summary of the vibrations assigned to the isotopomers of FCS.

A normal coordinate analysis can provide support

 	RCISD b)	FCS	F <sup>13</sup> CS	FC <sup>34</sup> S	F <sup>13</sup> C <sup>34</sup> S	
$\nu_1$	1429	1297.4	1259.3	1294.3	1256.2	÷.,
$2\nu_2$		910.3	904.6			
$\nu_2$	486	(456.9)	(451.0)			
V <sub>3</sub>	1013	917.9	895.3			
		(914.5)	(897.9)			
$v_1 + v_3$		2202.6	2143.7			
$2\nu_2 + \nu_3$		2195.7	2151.1			

Table 2

Vibrational frequencies of FCS (cm<sup>-1</sup>) in an argon matrix and from theory <sup>a</sup>)

a) Values in brackets indicate the deperturbed values used for normal coordinate analysis.

<sup>b)</sup> Ref. [5].

for the interpretation of the measured frequencies. since the force constants obtained can be compared with similar systems. In the case of FCS the vibrational frequencies in the 900  $cm^{-1}$  region are not suitable for direct use in a normal coordinate analysis, since the normal modes are perturbed by Fermi resonance. Using the frequencies and relative intensities of the observed peaks one can use first-order perturbation theory to obtain an estimate of the deperturbed, zero-order frequencies [29]. We performed this calculation and used the deperturbed values of  $\nu_2$  and  $\nu_3$  (table 2) together with the other measured frequencies as an input for a force constant fit with a normal coordinate analysis program [30]. The bond lengths  $r_{\rm CS} = 1.572$  Å,  $r_{\rm CF} = 1.305$  Å, and the angle  $\alpha_{\text{FCS}} = 131.8^{\circ}$  were taken from the ab initio calculations [5]. Since there is only one stable fluorine isotope, the input is restricted to the vibrations of only four distinct isotopic FCS species. Due to convergence problems, the best results could be achieved by keeping one of the interaction force constants fixed and adjusting iteratively the other five force constants. In view of this the results are not quite unique and unambiguous. A force field which satisfactorily reproduces the experimental data is shown in table 3 and compared with the CICS results

 Table 3

 Normal coordinate analysis of FCS

[9] and other related molecules in table 4. We have
obtained force fields, that are able to fit the fre-
quencies with similar accuracy, but with force con-
stants varying between 6.4 and 7.2 aJ Å <sup>-2</sup> for $f_{CS}$ and
between 5.7 and 6.1 aJ Å <sup>-2</sup> for $f_{CF}$ . The force field
with $f_{CF,FCS} = 0$ is selected because the interaction
constants of this force field are similar to the inter-
action constants of CICS. This force field also re-
produces some trends, that are observed in related
systems: The C-F bond of FCS (5.8 aJ $Å^{-2}$ ) is
weaker than that of the CF (7.4 aJ $Å^{-2}$ ) radical as
well as the C-F bond of $F_2CS$ (6.3 aJ Å <sup>-2</sup> ). This
weakening of the C-F bond has been observed for
FCO, and the same effect for the CCl bond is ap-
parent for ClCS and ClCO. The CS bond strength of
FCS (7.1 aJ $Å^{-2}$ ) is between the triple bond of CS
(8.5 aJ Å <sup>-2</sup> ) and the double bond of $F_2CS$ (6.5 aJ
Å <sup>-2</sup> ).

# 5. Conclusion

The FCS radical has been generated in solid argon matrix by a pulsed-jet DC discharge technique, and characterized spectroscopically by its infrared absorptions. The fundamental vibration  $v_1 = 1297.4$ 

Species	V	$\nu$ Frequency (cm <sup>-1</sup> )		Potential energy distribution						
		obs. a)	calc.	diff.	fcs	fcf	f <sub>FCS</sub>	fcs,cf	fcs,pcs	f <sub>cf,fcs</sub> <sup>a)</sup>
F <sup>12</sup> C <sup>32</sup> S	<b>V</b> 1	1297.4	1297.8	-0.4	50.5	64.2	0.2	-16.7	1.9	
	ν	914.5	914.6	-0.1	62.6	29.4	14.5	12.6	-19.2	
	v2	456.9	457.0	-0.1	0.8	8.9	96.8	-0.8	-5.7	
F <sup>12</sup> C <sup>34</sup> S	$\nu_1$	1294.3	1294.7	-0.4	49.2	65.3	0.2	-16.7	1.9	
	V <sub>3</sub>		907.7		64.1	28.2	15.0	12.5	- 19.7	
	$\nu_2$		453.9		0.7	9.0	96.3	-0.7	-5.3	
F <sup>13</sup> C <sup>32</sup> S	$\nu_1$	1259.3	1258.9	0.4	49.8	64.9	0.2	-16.7	1.9	
	V <sub>3</sub>	897.9	897.8	0.1	63.1	29.5	13.0	12.7	-18.2	
	$\nu_2$	<b>451</b> .0	450.9	0.1	1.2	8.2	9 <b>8.4</b>	-0.9	-6.8	
F <sup>13</sup> C <sup>34</sup> S	$\nu_1$	1256.2	1255.8	0.4	48.4	66.1	0.2	-16.6	2.0	
	V <sub>3</sub>		890.6		64.6	28.1	13.5	12.5	-18.8	
	<i>v</i> <sub>2</sub>		447.9		1.0	8.2	97.9	-0.8	-6.3	
Force constants b)					7.08	5.83	1.07	0 <b>.94</b>	0.87	0*)

<sup>a)</sup>  $f_{CF,FCS}$  was set to zero during iteration procedure.

<sup>b)</sup>  $f_{CS}$ ,  $f_{CF}$ ,  $f_{CS,CF}$  in aJ Å<sup>-2</sup>,  $f_{CS,FCS}$ ,  $f_{CF,FCS}$  in aJ Å<sup>-1</sup>,  $f_{FCS}$  in aJ.

Table 4	
Comparison of force constants *)	

	CS b)	CF »	CCl b)	FCS c)	CICS <sup>d</sup> )	F <sub>2</sub> CS <sup>e</sup> )	Cl <sub>2</sub> CS <sup>f</sup> )
la	8.49			7.08	7.73	6.508	6.312
fcf		7.42		5.83		6.28	
feet			3.95		2.92		3.213
fes.ca/fes.cr				0.94	0.89	0.866	0.729
facs/fres				1.07	1.01		
fes.cies/fes.fes				0.87	1.53		
fcci,cics/fcf,fcs				0.0 °)	0.04		
	CO b)	CF <sup>b)</sup>	CCl <sup>b)</sup>	FCO <sup>g)</sup>	CICO <sup>h)</sup>	F <sub>2</sub> CO <sup>i)</sup>	Cl <sub>2</sub> CO <sup>j</sup> )
fco	19.02			14.364	14.964	14.818	14.0
f <sub>CF</sub>		7.42		4.869		6.734	
fcci			3.95		1.173		3.24
fco,cci/fco,cf				1.305	1.413	1.095	0.85
faco/free				1.384	0.944		
fco.cico/fco.fco				0.380	0.026		
fcci,cico/fcf,fco				0.268	0.112		

<sup>a)</sup>  $f_{CS}$ ,  $f_{CF}$ ,  $f_{CS,CF}$  in aJ Å<sup>-2</sup>,  $f_{CS,FCS}$ ,  $f_{CF,FCS}$  in aJ Å<sup>-1</sup>,  $f_{FCS}$  in aJ.

b) Derived from gas-phase spectroscopic data, ref. [31].

<sup>c)</sup>  $f_{CF,FCS}$  was set to zero during fitting procedure.

<sup>d)</sup> Ref. [9]. <sup>e)</sup> Ref. [32]. <sup>f)</sup> Ref. [33]. <sup>g)</sup> Ref. [34].

<sup>h)</sup> Ref. [35]. <sup>i)</sup> Ref. [36]. <sup>j)</sup> Ref. [37].

cm<sup>-1</sup> and the Fermi resonance levels  $\nu_3$  and  $2\nu_2$  at 917.9 and 910.3 cm<sup>-1</sup>, respectively, are observed. The photodecomposition of FCS to F and CS using laser light near 440 nm has been observed and used in identifying weak combination bands at 2202.6 and 2195.7 cm<sup>-1</sup>. The vibrational assignments are supported by isotropic studies and by normal coordinate analysis. The results obtained are discussed and compared with similar molecules as well as with ab initio predictions.

#### Acknowledgement

This investigation was supported in part by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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