Difluorosilanethione $F_2Si{=}S$ by Flash Vacuum Thermolysis of $(F_3Si)_2S$ and by Reaction of SiS with F_2 – Matrix Studies and Ab initio Calculations

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Difluorosilanethione $F_2Si{=}S$ (**1**) has been synthesized by Flash Vacuum Pyrolysis of $(F_3Si)_2S$ at ≥ 500 °C and trapped in an Ar matrix. Furthermore, **1** has been obtained by codeposition of SiS and F_2/Ar and by pyrolysis of a matrix-isolated SiS_2–XeF_2 complex under cryogenic conditions. All six vibrational fundamentals of **1** have been observed in the matrix IR spectrum. Ab initio calculations at the MP2 and CCSD(T) levels using large basis sets have been performed. These calculations have guided the detection of **1** and the vibrational assignment. The best estimate of the structure of **1** with C_{2v} symmetry is: r(Si=S) 191.1(1) pm, r(SiF) 156.1(1) pm, ∠(FSiF) 103.3(2)°.

Our knowledge of molecular species exhibiting multiple bonds to silicon has expanded greatly over the past 20 years due to both experimental progress and improvements in theoretical methods. Above all, kinetic stabilization by bulky substituents at both sites of Si=Si,[1] Si=C,[2] and Si=Pn (Pn = N, P, As) linkages[3] has enabled the synthesis and isolation of numerous compounds that are thermally stable up to, and even above, room temperature and possess "formally" double bonded silicon atoms. However, chalcogeno derivatives $R^1R^2Si{=}Ch$, with Ch = O, S, etc., provide only the silicon site to accommodate bulky substituents, and it is not surprising that the first kinetically stabilized thioxosilane (silanethione[4]) that is stable at ambient temperature was made only recently.[5]

Monomeric silanones and silanethiones with trigonal planar geometry at silicon are kinetically unstable due to the lack of stabilization by bulky ligands. They have been frequently postulated as intermediates, mostly on the evidence of trapping experiments.[6] Only very few of these short-lived intermediates were, however, directly and unambiguously detected by spectroscopic methods, either in the gas phase, or in cryogenic matrices. Silanones $X_2Si{=}O$ with X = H,[7] F,[8] Cl,[9] and CH_3[10] have been the subject of quite a few successful experimental studies, and numerous theoretical studies have guided and confirmed experimental work.

Photolysis of matrix-isolated SiS in the presence of Cl_2[11] and HCl[12] has provided the first silanethiones, $Cl_2Si{=}S$ and Cl(H)Si=S, with trigonal Si coordination. Monomeric $(CH_3)_2Si{=}S$ (**3**), which was detected by photoelectron spectroscopy, has been generated in the gas phase by flash vacuum thermolysis (FVT) of the cyclotrimer (**4**) and of other organosilicon precursors.[13] However, attempts to synthesize the unsubstituted parent species $H_2Si{=}S$ by FVT of different precursors failed, and only the dehydrogenation product SiS has been observed.[14]

The present investigation adds to the limited list of unstabilized monomeric, four-atom silanethiones by describing $F_2Si{=}S$ (**1**). We report on the synthesis of this species by FVT of $(F_3Si)_2S$ (**2**). The unambiguous synthesis of the latter is also reported here for the first time. Alternatively, **1** can be made in analogy to $Cl_2Si{=}S$[11] by the action of F_2 on SiS under cryogenic conditions. High-level ab initio calculations, which guided the detection and support the characterization of **1** by matrix IR spectroscopy, will also be presented.

$F_2Si{=}S$	$(F_3Si)_2S$	$(CH_3)_2Si{=}S$	$[(CH_3)_2SiS]_3$
1	**2**	**3**	**4**

Experimental Results

It has been shown that at elevated temperature the cyclodimer of **3**, $[(CH_3)_2SiS]_2$ (**5**), is in equilibrium with the cyclotrimer **4**.[15] The photoelectron spectroscopic detection of **3** in the FVT of **4** proved that this equilibrium involves the monomer as an intermediate[13a] although it was not possible to trap **3** in an Ar matrix.[16]

$[(CH_3)_2SiS]_2$

5

We chose **1** as our target molecule because reactions analogous to the dehydrogenation of $H_2Si{=}S$,[14] or its isomerisation to yield the silylene HSi−SH, are unlikely to occur for **1** for thermodynamic reasons, the Si−F bond being particularly strong. It was therefore obvious to examine the thermal decomposition of $(F_2SiS)_2$ (**6**), which has been reported in the literature.[17] This promising precursor **6** was first mentioned by Gutmann et al.,[17a] who passed SiF_4

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over SiS_2 at 1000 °C in a quartz tube. Later, Aylett et al.[17b] claimed to have synthesized **6** by reaction of SiF_2I_2 with red HgS at room temperature.

$(F_2SiS)_2$
6

We have reexamined both reactions[18] and, although we were able to reproduce their general courses and the sparse spectroscopic data quoted, the products claimed to be **6** were in fact identified as $(F_3Si)_2O$[17a] and **2**,[17b] respectively. Our attempts to prepare **6** or other perfluorocyclosilthianes by reaction of the high temperature species SiF_2[19] with OCS or SPF_3 were unsuccessful in spite of the usefulness of OCS to transfer S onto matrix-isolated $SiCl_2$.[11]

Thermolysis of $F_3SiSSiF_3$

The thermolysis of noncyclic silthianes, which might be useful precursors for silanethiones, has not yet been investigated. We have found that in the condensed phase at room temperature **2** decomposes slowly to give SiF_4 and the trisildithiane $F_8Si_3S_2$ (**7**).[18] Upon prolonged storage at 20 °C, decomposition of **2** proceeds further to yield more SiF_4 and a solid deposit. The formation of **7** can be rationalized if **1** is considered to be an intermediate (Equations 1 and 2).

$$\mathbf{2} \rightarrow \mathbf{1} + SiF_4 \quad (1)$$

$$\mathbf{2} + \mathbf{1} \rightarrow \underset{\mathbf{7}}{(F_3SiS)_2SiF_2} \quad (2)$$

In order to detect any **1**, which is presumed to be formed according to Equation 1, we pyrolyzed 0.2% **2** seeded in Ar as a carrier gas at ≥ 500 °C in a quartz tube of 20 mm length and 10 mm inner diameter. The thermolysis products were condensed onto a cold window mounted at a distance of ca. 20 mm from the port of the oven. The deposit was first studied by infrared spectroscopy with a resolution of $0.5\ cm^{-1}$ in the $400-4000\ cm^{-1}$ region. The spectrum is displayed in Figure 1A.

Evidently the decomposition of **2** is almost quantitative. The spectrum is dominated by the very intense absorption of $^{28}SiF_4$ at $1023.3\ cm^{-1}$, accompanied by satellites of $^{29}SiF_4$ at $1014.4\ cm^{-1}$ (4.7%) and of $^{30}SiF_4$ at $1006.2\ cm^{-1}$ (3.1%). In addition there are two sharp absorptions at 995.7 and $969.1\ cm^{-1}$ with an intensity ratio of ca. 2:1 (Figure 1A). These absorptions are assigned to a hitherto unknown product. Both the wavenumbers of these two absorptions and their relative intensities agree perfectly with the ab initio predictions for the ν_1 and ν_4 absorption bands, respectively, of $F_2Si{=}S$ (**1**), Table 3.

Although lying in the recorded spectral region, the Si=S stretching vibration ν_2, expected near $640\ cm^{-1}$, was not found in this particular mid-infrared experiment (Figure 1A) with its predicted intensity being only 0.4% of ν_1.

In order to gather more information on the vibrational spectrum of **1** we have also investigated the matrix in the Far-IR range. Along with bands arising from the ν_4 vibration of SiF_4 and from F_3SiSH (**8**)[18] owing to some hydrolysis or minor contamination of **2**, we eventually detected absorptions at 337, 296, and $247\ cm^{-1}$ with relative intensities of 2.5:4.5:1 (Figure 1B). These absorptions were assigned to **1**. The intensities of these absorptions decreased uniformly on annealing the matrix to 42 K, while absorp-

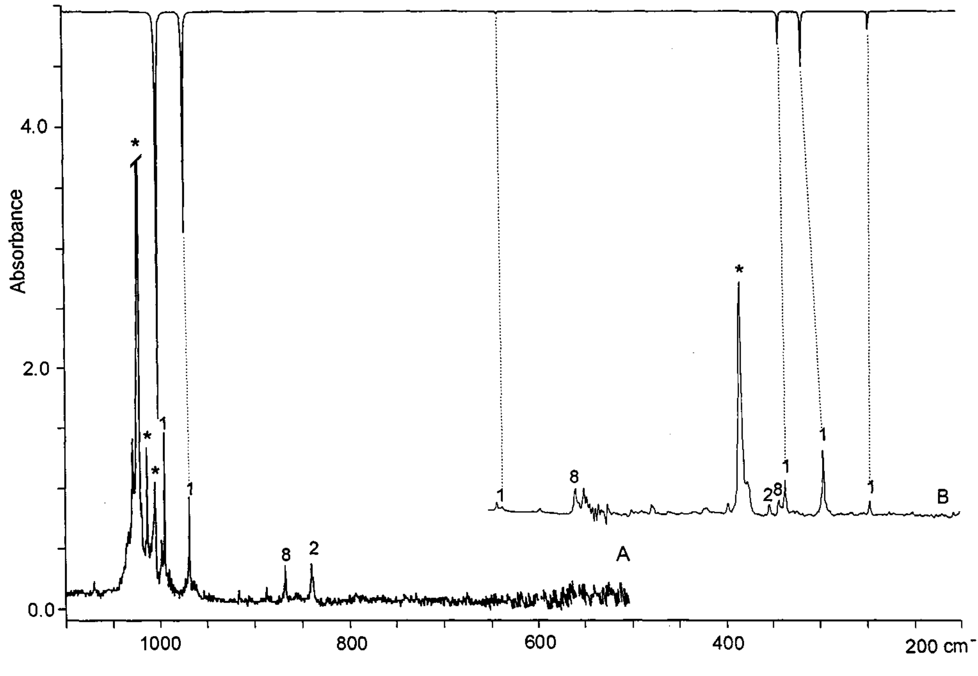

Figure 1. Matrix IR spectra of a deposit obtained by FVP of $(F_3Si)_2S$; A: $500-1100\ cm^{-1}$; B: $150-650\ cm^{-1}$; on top, pointing downwards, the ab initio predicted spectrum is shown; the labelling of the absorptions is: **1**: $F_2Si{=}S$; **2**: $(F_3Si)_2S$; **8**: F_3SiSH; SiF_4 peaks are marked by an asterisk

tions of the stable products persisted. UV irradiation of 193 and 248 nm did not change the spectrum.

F_3SiSH

8

The assignment in the 200−360 cm^{-1} range is not as straightforward as in the SiF stretching region because of partial overlap with bands arising from the precursor **2** and the hydrolysis product **8**. Matrix absorptions at 354.1 cm^{-1} (**2**) and 343.1 cm^{-1} (**8**) did not disappear upon annealing the matrix; they correspond to strong gas phase absorptions at 358 and 346 cm^{-1}, respectively, and are assigned to δ_s SiF_3.[18] The corresponding asymmetric deformations observed in the gas phase at 335 and 326 cm^{-1} (**2**) and 325 cm^{-1} (**8**) are weaker and occur in the matrix spectrum at 335.6 cm^{-1} and 322 cm^{-1} (broad, Figure 1). There is a coincidence of the 335.6 cm^{-1} band with that of **1** at 336.5, hence upon annealing of the matrix the band at 337 cm^{-1} is only weakened while those at 296 and 247 cm^{-1} disappear entirely.

Comparison of the matrix spectra before and after annealing reveals a weak feature at 638 cm^{-1} (Figure 1B) that must be due to an unstable intermediate. On the basis of the ab initio calculations (Table 3; see below) we definitely assign this feature to the Si=S stretching vibration. On the other hand, new weak absorptions at 1004, 981.5, 862.2, and 858.0 cm^{-1} (ν SiF) and 561 and 557 cm^{-1} (ν SiS) appear in the annealed spectrum; these have not yet been assigned but might be due to oligomers of **1**.

Reaction of Matrix-Isolated SiS with F_2

In analogy to the synthesis of Cl_2SiS from SiS and Cl_2[11] co-condensation of SiS with F_2 and Ar promises access to **1**. IR spectra of these deposits (Figure 2) revealed, in addition to absorptions of SiS (739 cm^{-1}) and its dimer and its trimer, some red-shifted bands at 728 cm^{-1}, which are assigned to association products of molecular SiS with F_2.

Furthermore, three additional absorptions at 995.6, 969.1, and 296.5 cm^{-1} were observed that, owing to their invariant relative intensities, were assigned to the same, novel short-lived species. Of these, the two strong absorptions > 900 cm^{-1} are likely to be due to SiF stretching vibrations of tetravalent silicon bonded to two or more fluorine atoms. Respective absorptions of Si^{II} fluorides should occur at lower wavenumbers, 840−869 cm^{-1}.[21] One further band at 903 cm^{-1} (Figure 2) has not yet been assigned.

Both the wavenumbers and intensities of the three absorptions mentioned above are in perfect agreement with those that had been assigned in the pyrolysis experiment to **1** on the basis of ab initio calculations. Once again the SiS stretching vibration of **1**, predicted to be near 640 cm^{-1} with very low IR intensity and observed in the spectrum shown in Figure 1B, was too weak to be detected. In addition to the bands of **1**, SiF stretching absorptions of the stable product **8** (986.6 and 865.2 cm^{-1}) and SiF_4 (1023 and 386.7 cm^{-1}) were also observed.

In order to support the assignment of the absorptions of **1** we condensed gaseous SiS with XeF_2 and Ar and photolyzed the resulting deposit with radiation from a high pressure Hg lamp. This experiment was performed by passing Ar over crystalline XeF_2 at −40°C and co-condensing this mixture with SiS. The IR spectrum of this deposit revealed only the presence of SiS, XeF_2 and a band at 725 cm^{-1} assigned to a SiS−XeF_2 complex. After photolysis, absorptions similar to those observed with a SiS/F_2 mixture appeared and were assigned to **1**. We did not find the SiS stretching vibration of **1** in this experiment. In order to confirm our observation of this vibration (Figure 1B) we plan to study the SiS−Ar/F_2 system by Raman spectroscopy.

Ab initio Calculations

Theoretical Methods

Quantum-chemical calculations were carried out at the correlated levels of second-order Møller−Plesset perturbation theory (MP2)[22] and coupled cluster theory with single and double excitations[23] augmented by a perturbational estimate of the effects of connected triple excitations [CCSD(T)].[24] These calculations were performed with GAUSSIAN94[25] and MOLPRO94.[26][27]

The correlation-consistent polarized valence basis sets (cc-pVXZ)[28][29] were used throughout, supplemented as suggested recently[30] to take into account core polarization effects in the case of second-row atoms. Specifically, three different basis sets were employed: the first one denoted as VTZ+1 is derived from the triple-zeta cc-pVTZ basis[28][29] by adding a single set of d functions for Si and S[30] whose exponents equal the highest d exponent in the corresponding cc-pV5Z basis.[31] Analogously, the second basis (VQZ+1) is obtained from the quadruple-zeta cc-pVQZ basis set[28][29] by adding the same high-exponent d functions for Si and S.[30][31] Replacement of the cc-pVQZ functions for F and S by the corresponding augmented sets (aug-cc-pVQZ)[29][32] generates the third basis (AVQZ+1), which contains low-exponent diffuse functions to account for the electronegative character of F and S.

Spherical harmonics were used throughout. Unless stated otherwise, the fluorine 1s-like and the silicon and sulfur 1s2s2p-like core molecular orbitals were always required to remain doubly occupied (frozen core approximation). Nondynamical electron correlation is not overly important in F_2SiS, as judged from the coupled cluster T_1 diagnostic,[33][34] which is 0.013 for all three basis sets at the corresponding CCSD(T) minimum energy structures. Therefore, **1** is expected to be well described by single reference coupled cluster wavefunctions. The molecules SiS and SiF_2 were also treated (see below). The T_1 diagnostic for SiF_2 is about 0.014, i.e. similar to the value of F_2SiS, and 0.021 for SiS. Although this latter value is already critical in the sense that results from single-reference electron correlation methods limited to single and double excitations (e.g. MP2, CCSD) should be viewed with caution, CCSD(T) still performs reasonably well.[34]

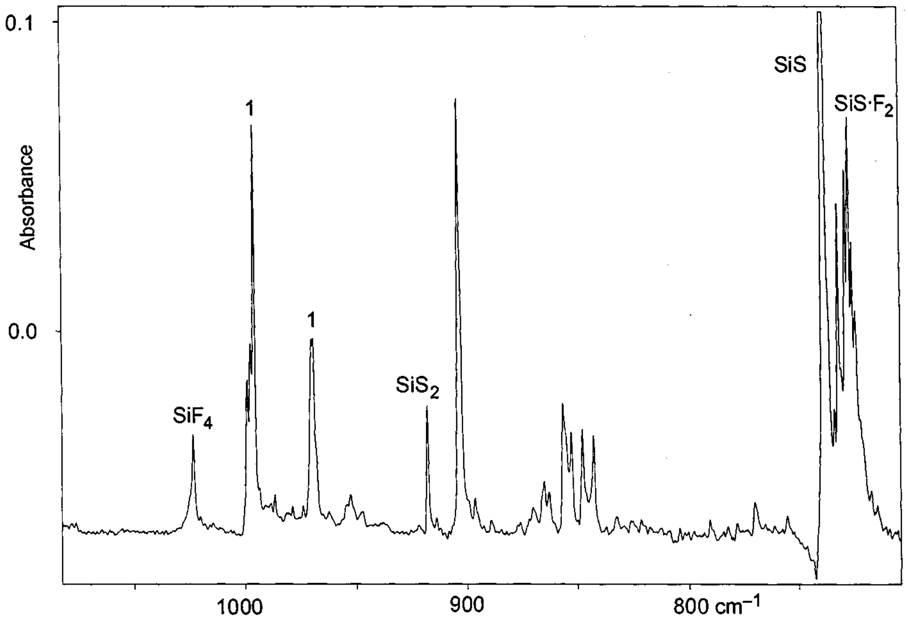

Figure 2. IR spectrum in the 700−1200 cm^{-1} range of the deposit formed by co-deposition of SiS and F_2/Ar; **1**: $F_2Si{=}S$

The molecular geometry of **1** was optimized within the constraint of C_{2v} point group symmetry. For the purpose of comparison, the molecular structures of SiS ($C_{\infty v}$) and SiF_2 (C_{2v}) were also optimized. Analytic energy gradients, as implemented in the GAUSSIAN94 program,[25] were used at the MP2 level of theory, and numerical gradients were employed at the CCSD(T) level with MOLPRO94.[26][27] The largest internal gradient components at the stationary points did not exceed $3 \cdot 10^{-5}$ au.

At the computed equilibrium geometries, harmonic force fields were evaluated either analytically in Cartesian coordinates (MP2/VTZ+1)[25] or numerically in symmetry-adapted internal coordinates from energies[26] (step sizes 0.02 Bohr for bond lengths and 1° for bond angles). The normal modes and the harmonic vibrational frequencies were obtained in the usual manner.[35][36] At the CCSD(T) level, electric dipole moments were determined as numerical derivatives of the potential energy with respect to a finite field component (0.003 au) using the MOLPRO94 program.[26]

The following symmetry coordinates were chosen to represent the quadratic CCSD(T)/VQZ+1 force field:

$S_1(a_1) = 2^{-1/2}\,(r_1 + r_2)$
$S_2(a_1) = R$
$S_3(a_1) = 6^{-1/2}\,(2\alpha - \beta_1 - \beta_2)$
$S_4(b_1) = 2^{-1/2}\,(r_1 - r_2)$
$S_5(b_1) = 2^{-1/2}\,(\beta_1 - \beta_2)$
$S_6(b_2) = \gamma$

where r_1 and r_2 are the two SiF bond lengths, R is the Si−S bond length, α is the F−Si−F bond angle, β_1 and β_2 are the two F−Si−S bond angles, and γ is the out-of-plane angle between the Si−S bond and the SiF_2 plane.

For comparison with the present experimental data, the cubic and quartic force fields of **1** are required to deduce theoretical values for the fundamental vibrational frequencies. The MP2/VTZ+1 cubic and quartic normal coordinate force constants that are not reported explicitly were determined with the use of a finite difference procedure[37] involving displacements along reduced normal coordinates (step size $\Delta q = 0.05$) and the calculation of analytic second derivatives (relative precision $\varepsilon < 10^{-7}$) at these displaced geometries. At the MP2/VTZ+1 equilibrium geometry of **1**, the Cartesian gradient components did not exceed $5 \cdot 10^{-7}$ au. The anharmonicity corrections to the harmonic vibrational wavenumbers were computed from the theoretical anharmonicity constants using standard formulas based on second-order rovibrational perturbation theory.[38][39]

Results and Discussion

Table 1 shows the computed equilibrium geometries, electric dipole moments and atomic charges from a natural population analysis[25] of F_2SiS. As expected, the enlargement of the basis set from VTZ+1 to VQZ+1 shortens the SiF bonds slightly (0.13−0.18 pm) and the SiS bond somewhat more (0.34−0.49 pm) while the FSiF bond angle increases by 0.12−0.15°. The addition of diffuse functions at F and S (AVQZ+1) leads to almost negligible changes in the structural parameters: the bond lengths increase by less than 0.1 pm and the FSiF bond angle decreases by less than 0.05°. For a given basis, CCSD(T) predicts a longer SiS bond and shorter SiF bonds than MP2, but the differences remain small (0.23−0.38 pm), and the computed bond angles are almost identical. Correlating all electrons at the CCSD(T)/VQZ+1 level shortens the SiS and SiF bonds considerably, viz. by 0.85 pm and 0.83 pm, respectively, whereas the FSiF bond angle is only slightly affected (+0.07°). The computed values for the electric dipole moment of **1** are close to 1.2 Debye (see Table 1). The present

Table 1. Computed equilibrium geometries and electric dipole moments of F_2SiS[a]

Constant	MP2			CCSD(T)				Best estimate[c]
	VTZ+1	VQZ+1	AVQZ+1	VTZ+1	VQZ+1	VQZ+1(ae)[b]	AVQZ+1	
SiS	192.25	191.91	191.96	192.63	192.14	191.29	192.20	191.1(1)
SiF	157.28	157.15	157.22	157.02	156.84	156.01	156.90	156.1(1)
FSiF	103.17	103.29	103.26	103.12	103.27	103.34	103.23	103.3(2)
μ_e	1.275	1.222	1.194	1.205	1.181	1.178	1.150	1.19(10)[d]

[a] Bond lengths in pm, bond angles in degrees, dipole moments in Debye. − [b] ae = all electrons correlated. − [c] See text. Estimated errors in parentheses. − [d] CCSD(T)/AVQZ+1 value at the best estimated molecular geometry. The dipole vector is directed from S to Si. A natural population analysis (MP2/VTZ+1)[25] revealed the following atomic charges (atomic units): Si +1.903, S −0.678, F −0.613.

best value [CCSD(T)/AVQZ+1] is believed to be accurate to about 0.1 Debye.

The calculated geometrical data of F_2SiS may be improved by taking into account the errors that appear in analogous calculations for the related molecules SiS and SiF_2, where accurate experimental equilibrium geometries are known.[40][41] For this purpose Table 2 presents computed and experimental equilibrium structures for both species. It is seen that CCSD(T)/VQZ+1 overestimates the bond lengths in SiS and SiF_2 by as much as 0.97 pm and 0.69 pm, respectively, if inner-shell contributions to the electron correlation are neglected. As in the case of **1**, taking core correlation into account [CCSD(T)/VQZ+1(ae)] leads to a considerable contraction of the bond lengths in SiS (−0.69 pm) and SiF_2 (−0.76 pm) while the bond angle in SiF_2 changes only moderately (+0.12°). Consequently, the all-electron bond lengths in SiS and SiF_2 are much closer to the experimental values than those obtained by correlating only the valence electrons (see Table 2). If the errors in the calculated bond lengths of these two molecules (with and without the frozen core approximation) are used to correct the corresponding data for the target molecule **1**, we arrive at three consistent estimates for the equilibrium distances in F_2SiS. The best estimate (see Table 1) is the average of these three individual estimates, which lie within the quoted uncertainty. Since the calculated FSiF bond angles in **1** are quite similar at all levels, we have adopted the CCSD(T)/VQZ+1 value (103.3°) as our best estimate and have assigned an error bar (0.2°) that covers all theoretical values of this angle (see Table 1).

Table 3 reports theoretical results for the fundamental vibrational wavenumbers of F_2SiS and compares them with their experimental counterparts determined in this work. The theoretical values were derived from the corresponding harmonic wavenumbers obtained at a given level, by adding the anharmonicity corrections from MP2/VTZ+1 calculations. At this level there are no complications due to anharmonic resonances, except for $\nu_2/2\nu_6$ where perturbationally and variationally determined Fermi shifts due to this cubic interaction differ by about 4 cm^{-1}. Consequently, all theoretical Fermi shifts of ν_2 (ranging from 3.5−6.4 cm^{-1}) were obtained by matrix diagonalization using harmonic wavenumbers from the given level of theory and the coupling element W_{266} = 10.2 cm^{-1} from MP2/VTZ+1. The calculated fundamental wavenumbers are quite stable with respect to the employed basis sets, i.e. the corresponding data differ at most by 5 cm^{-1}. Comparing CCSD(T) with the associated MP2 data, the differences do not exceed 9 cm^{-1} in absolute value. Generally, the calculated wavenumbers agree with experiment to within 9 cm^{-1}, with the exception of the out-of-plane vibrational mode where the differences range from 11−20 cm^{-1}. From a theoretical point of view, our best data are those from CCSD(T)/VQZ+1 where the rms deviation from experiment is 7 cm^{-1}. This agreement between theory and experiment is as good as can be expected,[34] especially when taking into account that the experimental vibrational wavenumbers have been measured in an argon matrix (15 K) and not in the gas phase. Therefore, our calculations are fully consistent with the assignment of the measured bands to F_2SiS. Further support for this assignment comes from the theoretical (MP2/VTZ+1) intensity pattern of the infrared absorptions, which is in very good agreement with the experimental relative intensities (see Table 3).

In Table 4 the CCSD(T)/VQZ+1 harmonic symmetry force constants of **1** are listed. Not surprisingly, this force field is dominated by the diagonal stretching constants F_{11} (SiF_2 sym. str.), F_{44} (SiF_2 asym. str.), and F_{22} (SiS str.). The associated potential energy distribution (PED) matrix reveals a significant coupling only between the symmetric SiF_2 (S_1) and the SiS (S_2) stretching coordinates (ν_1: 68% SiF_2, 28% SiS; ν_2: 28% SiF_2, 69% SiS), whereas the other

Table 2. Computed and experimental equilibrium geometries[a] of SiS and SiF_2

Molecule	Constant	CCSD(T) VQZ+1	CCSD(T) VQZ+1(ae)[b]	CCSD(T) AVQZ+1	Exp.[c]
SiS	SiS	193.90	193.21	193.96	192.9264(2)
SiF_2	SiF	159.70	158.94	159.85	159.01(1)
	FSiF	100.86	100.98	100.66	100.77(2)

[a] Bond lengths in pm, bond angles in degrees. − [b] ae = all electrons correlated. − [c] Refs.[40][41] for SiS and SiF_2, respectively.

Table 3. Fundamental vibrational wavenumbers (cm^{-1}) of F_2SiS

Mode	Exp.[a]	MP2			CCSD(T)	
		VTZ+1[b]	VQZ+1[c]	AVQZ+1[c]	VTZ+1[c]	VQZ+1[c,d]
a_1 $\nu_s(SiF_2)$	996 (2.60)	1003 (262)	1004	1000	1001	1005 (1015)
$\nu(SiS)$	638 (0.02)	647[e] (1)	647[e]	646[e]	638[e]	641[e] (643)
$\delta(SiF_2)$	337 (0.30)	339 (25)	338	336	340	339 (340)
b_1 $\nu_{as}(SiF_2)$	969 (1.30)	967 (142)	970	965	972	977 (988)
$\rho(SiF_2)$	247 (0.12)	247 (10)	248	247	245	247 (248)
b_2 $\gamma(SiF_2)$	296 (0.54)	316 (33)	313	312	309	307 (308)

[a] Extinction in parentheses. − [b] Infrared band intensities (km/mol) in parentheses (double harmonic approximation). − [c] Anharmonicity corrections from MP2/VTZ+1. − [d] Harmonic wavenumbers in parentheses. − [e] Including the shift due to the $\nu_2/2\nu_6$ Fermi interaction. These shifts have been calculated variationally using harmonic wavenumbers from the indicated level of theory and the interaction constant $W_{266} = 10.2\ cm^{-1}$ (MP2/VTZ+1).

Table 4. Computed[a] harmonic symmetry force constants F_{ij}[b] of F_2SiS

	i	j	F_{ij}		i	j	F_{ij}
a_1	1	1	6.437	b_1	4	4	5.973
	1	2	0.170		4	5	0.152
	1	3	0.263		5	5	0.511
	2	2	5.167				
	2	3	−0.123	b_2	6	6	0.460
	3	3	0.833				

[a] CCSD(T)/VQZ+1. − [b] Units are consistent with energies in aJ, bond lengths in 100 pm, and angles in radians.

normal modes correspond to almost pure symmetry coordinates (dominant PED contributions to $\nu_3 - \nu_6$: above 95%).

Discussion

The present study establishes the existence of hitherto unknown **1** under cryogenic conditions. We have been able to synthesize **1** by FVT of **2**, by reaction of SiS with F_2 in an Ar matrix, and by photolysis of a matrix isolated $SiS-XeF_2$ complex. All vibrational fundamentals of **1** were observed. These fundamentals were assigned on the basis of high-level ab initio calculations.

Owing to the strong mixing of the S_1 and S_2 coordinates, the vibration with predominantly Si=S stretching character at 638 cm^{-1} is much lower than those of $Cl_2Si=S$ (805.6 cm^{-1})[11] and Cl(H)Si=S (775 cm^{-1})[12]. In matrix-isolated Si=S this vibration lies at 739.1 cm^{-1}.[42] The Si=S stretching force constant of **1** obtained by quantum chemical calculations, 5.167 Ncm^{-1} (Table 4), exceeds that of $Cl_2Si=S$ (4.90 Ncm^{-1})[11] and Cl(H)Si=S (4.83 Ncm^{-1})[12] as well as those of SiS and SiS_2, 4.9 Ncm^{-1}.[43] The C=S stretching force constants of related CS (8.5 Ncm^{-1}), CS_2 (7.7 Ncm^{-1}) and F_2CS (6.7 Ncm^{-1})[44] vary much more.

Difluorosilanethione has the shortest SiS bond and largest SiS stretching force constant so far determined. The "best" prediction of the SiS bond length in **1**, 191.1 pm (Table 1), is significantly shorter than those of the two independent $2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2[2,4,6\text{-}(Me_2CH)_3\text{-}C_6H_2]Si=S$ molecules as determined by single crystal X-ray diffraction, 194.8(4) and 195.2(4) pm.[5] It is also shorter than in SiS 192.9264(2) pm.[40] The SiS single bond length in $H_3SiSSiH_3$ is considerably longer, 213.6(2) pm.[45]

Experimental Section

Synthesis of $(F_3Si)_2S$ (2):[18] 8.6 g (39.2 mmol) of SiF_3I and 16 g (69 mmol) of HgS were sealed together in a pyrex tube with a volume of 13.3 mL and allowed to react for 7 d at room temperature. Volatile products were purified by fractionated distillation using a low temperature column to yield 0.7 g (6.7 mmol) of SiF_4, 1.7 g (7.9 mmol) of SiF_3I, 2.1 g (10.7 mmol) of **2**, and 0.5 g of less volatile products containing Si and S. The purity of **2**, b.p. −3°C, was checked by IR and ^{19}F-NMR spectroscopy.

Thermolysis of 2: Matrix isolation experiments were performed using standard techniques with an APD CSW-202 Displex closed-cycle He cryostat. Matrices were produced by deposition of Ar (Messer Griesheim, 99.9999%) at a rate of 1.5 sccm/min on a CsI window at 15−20 K. Infrared spectra were recorded with a resolution of 0.5 cm^{-1} employing a Bruker IFS 66 FTIR spectrometer equipped with a KBr beam splitter and a MCT detector. The Far IR experiments were performed using polyethylene windows, a Mylar beam splitter and a DTGS detector. Irradiations were carried out with an Excimer Laser (Lambda Physics COMPex 100, ArF 193 nm, KrF 248 nm).

Reaction of Matrix-Isolated SiS with F_2 or with XeF_2: Experiments were carried out using a Leybold RGD 510 closed cycle cryostat. Matrices were condensed onto a cold copper mirror. Spectra were recorded in absorption by means of a reflection unit using a Bruker IFS 113v FTIR spectrometer. A constant flow of molecular SiS was produced by passing H_2S over solid silicon resistively heated to 1200°C in an alumina tube. Fluorine was stored and mixed with Ar in passivated stainless steel containers. Photolysis (310 nm interference filter) was performed with a high pressure Hg lamp (Osram HBO 200).

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[1] R. Okazaki, R. West, *Adv. Organomet. Chem.* **1996**, *39*, 231−273.

[2] A. G. Brook, M. A. Brook, *Adv. Organomet. Chem.* **1996**, *39*, 71−158.

[3] M. Driess, *Adv. Organomet. Chem.* **1996**, *39*, 193−229.

[4] According to IUPAC nomenclature compounds with Si=S double bonds are named "thioxosilanes" or "silylidenesulfanes". However, in the relevant literature the name "silanethiones" is common.

[5] [5a] H. Suzuki, N. Tokitoh, R. Okazaki, S. Nagase, M. Goto, *J. Am. Chem. Soc.* **1998**, *120*, 11096−11105. − [5b] H. Suzuki, N. Tokitoh, S. Nagase, R. Okazaki, *J. Am. Chem. Soc.* **1994**, *116*, 11578−11579.

[6] [6a] G. Raabe, J. Michl in *The Chemistry of Organic Silicon Compounds*, Part 2 (Eds.: S. Patai, Z. Rappoport), John Wiley, New York, **1989**, pp. 1015−1142. − [6b] P. Lu, J. K. Paulasaari, W. P. Weber, *Organometallics* **1996**, *15*, 4649−4652. − [6c] J. Chojnowski, W. Stanczyk, *Adv. Organomet. Chem.* **1990**, *30*, 243−307. − [6d] N. C. Norman, *Polyhedron* **1993**, *12*, 2431−2446.

[7] [7a] S. Bailleux, M. Bogey, C. Demuynck, J.-L. Destombes, A. Walters, *J. Chem. Phys.* **1994**, *101*, 2729−2733. − [7b] R. J. Glinski, J. L. Gole, D. A. Dixon, *J. Am. Chem. Soc.* **1985**, *107*, 5891−5894. − [7c] R. Whithnall, L. Andrews, *J. Am. Chem. Soc.* **1985**, *107*, 2567−2568. − [7d] R. Whithnall, L. Andrews, *J. Phys. Chem.* **1985**, *89*, 3261−3268. − [7e] R. Srinivas, D. K. Böhme, D. Sülzle, H. Schwarz, *J. Phys. Chem.* **1991**, *95*, 9836−9841.

[8] H. Schnöckel, *J. Mol. Struct.* **1980**, *65*, 115−123.

[9] H. Schnöckel, *Angew. Chem.* **1978**, *90*, 638−639.

[10] V. N. Khabashesku, Z. A. Kerzina, E. G. Baskir, A. K. Maltsev, O. M. Nefedov, *J. Organomet. Chem.* **1988**, *347*, 277−293.

[11] H. Schnöckel, H.-J. Göcke, R. Köppe, *Z. Anorg. Allg. Chem.* **1989**, *578*, 159−165.

[12] R. Köppe, H. Schnöckel, *Z. Anorg. Allg. Chem.* **1992**, *607*, 41−44.

[13] [13a] C. Guimon, G. Pfister-Guillouzo, H. Lavayssière, G. Dousse, J. Barrau, J. Satgé, *J. Organomet. Chem.* **1983**, *249*, C17−C20. − [13b] V. Lefevre, J.-L. Ripoll, *Phosphorus Sulfur Silicon* **1997**, *120*/*121*, 371−372.

[14] A. Chivé, V. Lefevre, A. Systermans, J. L. Ripoll, M. Bogey, A. Walters, *Phosphorus Sulfur Silicon* **1994**, *91*, 281−284.

[15] [15a] A. Haas, *Angew. Chem.* **1965**, *77*, 1066−1075. − [15b] K. Moedritzer, *J. Organomet. Chem.* **1970**, *21*, 315−320.

[16] L. G. Gusel'nikov, V. V. Volkova, V. G. Avakyan, N. S. Nametkin, M. G. Voronkov, S. V. Kirpichenko, E. N. Suslova, *J. Organomet. Chem.* **1983**, *254*, 173−187.

[17] [17a] V. Gutmann, P. Heilmeyer, K. Utvary, *Monatsh. Chem.* **1961**, *92*, 942−943. − [17b] B. J. Aylett, I. A. Ellis, J. R. Richmond, *J. Chem. Soc., Dalton Trans.* **1973**, 981−987.

[18] H. Beckers, H. Bürger, to be published.

[19] J. L. Margrave, P. W. Wilson, *Acc. Chem. Res.* **1971**, 145−151.

[20] D. W. Kohn, H. Clausenberg, P. Chen, *Rev. Sci. Instrum.* **1972**, *63*, 4003−4005.

[21] J. W. Hastie, R. H. Hauge, J. L. Margrave, *J. Am. Chem. Soc.* **1969**, *91*, 2536−2538.

[22] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618−622.

[23] G. D. Purvis III, R. J. Bartlett, *J. Chem. Phys.* **1982**, *76*, 1910−1918.

[24] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479−483.

[25] M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, *GAUSSIAN94*, Revisions D.4 and E.2, Gaussian Inc., Pittsburgh, **1995**.

[26] *MOLPRO94* is a package of ab initio programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. M. Pitzer, A. J. Stone, and P. R. Taylor.

[27] C. Hampel, K. A. Peterson, H.-J. Werner, *Chem. Phys. Lett.* **1992**, *190*, 1−12.

[28] T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007−1023.

[29] D. E. Woon, T. H. Dunning, Jr., *J. Chem. Phys.* **1993**, *98*, 1358−1371.

[30] J. M. L. Martin, O. Uzan, *Chem. Phys. Lett.* **1998**, *282*, 16−24.

[31] D. E. Woon, T. H. Dunning, Jr., *J. Chem. Phys.* **1995**, *103*, 4572−4585.

[32] R. A. Kendall, T. H. Dunning, Jr., R. J. Harrison, *J. Chem. Phys.* **1992**, *96*, 6796−6806.

[33] T. J. Lee, P. R. Taylor, *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199−207.

[34] T. J. Lee, G. E. Scuseria in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy* (Ed.: S. R. Langhoff), Kluwer, Dordrecht, **1995**, pp. 47−108.

[35] E. B. Wilson, Jr., J. C. Decius, P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, **1955**.

[36] S. Califano, *Vibrational States*, Wiley, New York, **1976**.

[37] W. Schneider, W. Thiel, *Chem. Phys. Lett.* **1989**, *157*, 367−373.

[38] I. M. Mills in *Molecular Spectroscopy: Modern Research* (Eds.: K. N. Rao, C. W. Mathews), vol. 1, Academic, New York, **1972**, pp. 115−140.

[39] D. A. Clabo, Jr., W. D. Allen, R. B. Remington, Y. Yamaguchi, H. F. Schaefer III, *Chem. Phys.* **1988**, *123*, 187−239.

[40] E. Tiemann, H. Arnst, W. U. Stieda, T. Törring, J. Hoeft, *Chem. Phys.* **1982**, *67*, 133−138.

[41] H. Shoji, T. Tanaka, E. Hirota, *J. Mol. Spectrosc.* **1973**, *47*, 268−274.

[42] R. M. Atkins, P. L. Timms, *Spectrochim. Acta A* **1977**, *33*, 853−857.

[43] H. Schnöckel, R. Köppe in *Organosilicon Chemistry: From Molecule to Materials*, vol. I (Eds.: P. Weis, N. Auner), Verlag Chemie, **1994**, p. 147−153.

[44] A. Haas, H. Willner, H. Bürger, G. Pawelke, *Spectrochim. Acta A* **1977**, *33*, 937−945.

[45] A. Almenningen, L. Fernholt, H. M. Seip, *Acta Chem. Scand.* **1968**, *22*, 51−58.

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