

TABLE VI
COMPARISON OF CHLORANIL^a AND TCNE-METHOXYBENZENE COMPLEXES

Donor	Acceptor					
	Chloranil			TCNE		
	$\Delta\bar{\nu}$ (Benz-I), ^b 10 ³ cm. ⁻¹	Cor. by eq. 10	ϵ^* methoxy, 10 ³ cm. ⁻¹	γ^* methoxy, 10 ³ cm. ⁻¹	ϵ^* methoxy, 10 ³ cm. ⁻¹	γ^* methoxy, 10 ³ cm. ⁻¹
Anisole	7.3	8.4	7.9	0.5	7.8 ± 0.3	-0.35 ± 0.25
<i>o</i> -Dimethoxybenzene ^c	10.3	11.8	7.6	0.2	7.7 ± 0.35	-0.5 ± 0.25
<i>m</i> -Dimethoxybenzene ^d	10.2	11.7	5.0	0.7	5.8 ± 1.3	-0.5 ± 0.3
<i>p</i> -Dimethoxybenzene	11.3	13.0	6.3	0.25	6.1 ± 0.35	-0.3 ± 0.15
1,3,5-Trimethoxybenzene	9.1	10.5	6.0	(Value 0.5 used)	7.1	0.5

^a See ref. 7. ^b $\Delta\bar{\nu}$ (Benz-I): separation of first c.-t. energy in methoxybenzene-chloranil complexes from the c.-t. energy of the benzene-chloranil complex. ^c Measured in this work: two c.-t. bands at 518 and \sim 386 m μ overlapping. ^d Two very strongly overlapping transitions and only approximate values used.

tions $h\nu_{CT}(I,II) = aI_D(I,II)$ which were made in our calculation of γ_S^* are inaccurate, particularly for the one involving the second c.-t. band, and a more exact expression is required. The most complete description of $h\nu_{CT}$ is given by eq. 2. Unfortunately, not enough data are available as yet to make use of this equation for a more precise, quantitative evaluation of our results.

Qualitatively, however, it is important to realize that simple approximations which described first c.-t. transitions quite accurately are insufficient for the description of second transitions. This is also evident from Hückel calculations on the molecular orbital energies of methoxybenzenes and subsequent comparison of their c.-t. energies with a number of acceptors.²⁸ A good linear correlation was found between the energies of the highest filled methoxybenzene orbitals with the first c.-t. energies of their complexes with all acceptors considered. With TCNE, they also compared the energies of the second highest filled donor MO's with the energies of the corresponding second c.-t. absorptions. In this case, no good linear correlation was obtained. Even though this correlation is improved when our analyzed c.-t. values (Table I) are used, the second c.-t. energies still do not fall on the same line with the first. Whether or not this is largely

(28) A. Zweig, J. E. Lehnson, and M. A. Murray, *J. Am. Chem. Soc.*, **85**, 3933 (1963).

the result of poor second MO energies, there can be little doubt that some of the irregularities derive from the c.-t. process.

If the complexes have structures similar to those shown in Fig. 1 and 2, then the configurations contributing primarily to the first c.-t. transitions are orthogonal to those contributing primarily to the second transitions. For benzene donor cations with electron-releasing substituents the ground state is expected to be antisymmetric for mono- and disubstituted isomers, while for tetra- and pentasubstituted isomers the symmetric orbital should be the lowest. Therefore, the first c.-t. band of the former derives principally from structures R_y (Fig. 1), that of the latter from structures R_x (Fig. 2). The opposite applies to configurations contributing to the second charge-transfer absorptions. Thus, a change in complex structure with increasing donor substitution is expected for each c.-t. band.

Apparently, this theoretically expected changeover in complex geometry does not show up in the experimental first c.-t. energies (at least of the methoxybenzenes). The second c.-t. energies cannot be correlated at present.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

The Mass and Microwave Spectra, Structures, and Dipole Moments of the Isomers of Sulfur Monofluoride¹

BY ROBERT L. KUCZKOWSKI²

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Two isomers of S₂F₂ were prepared by heating AgF and S. The relative mass spectral cracking patterns of both isomers are reported. For one isomer, microwave transitions for the S³²=S³²F₂, S³²=S³⁴F₂, and S³⁴=S³²F₂ species were obtained. The structure was determined to be pyramidal S=SF₂ with $d(SS) = 1.860 \pm 0.015$ Å., $d(SF) = 1.598 \pm 0.012$ Å., $\angle SSF = 107.5 \pm 1^\circ$, and $\angle FSF = 92.5 \pm 1^\circ$. The dipole moment was 1.03 ± 0.03 D. For the second isomer, microwave transitions for the FS³²S³²F and FS³²S³⁴F species were obtained. The structure was determined to be nonplanar chain FSSF with $d(SS) = 1.888 \pm 0.01$ Å., $d(SF) = 1.635 \pm 0.01$ Å., $\angle FSS = 108.3 \pm 0.5^\circ$, and the dihedral angle = $87.9 \pm 1.5^\circ$. The dipole moment was 1.45 ± 0.02 D. A discussion of the observed structural parameters for both isomers is given.

Introduction

The earlier reports in the literature concerning S₂F₂ presented some conflicting data and gave rise to general

(1) This work was supported by a grant extended to Harvard University by the Office of Naval Research. Reproduction in whole or part is permitted for the U. S. Government.

(2) (a) Standard Oil of California Predoctoral Fellow 1963-1964; (b) National Bureau of Standards, Washington, D. C.

skepticism concerning this compound.³ Because of an interest in this laboratory in the structure of some similar molecules, notably F₂O₂,⁴ we were prompted to re-investigate S₂F₂ with the hope of unambiguously characterizing it as well as determining its structural param-

(3) See footnotes 2-9 in ref. 5 of this paper.

(4) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).

eters. As a result, in two recent communications we have shown by microwave and mass spectroscopy that it exists as two isomers with pyramidal $S=SF_2$ and non-planar chain FSSF structures.^{5,6} In concurrent reports, Seel, *et al.*, have also identified these isomers primarily by infrared and mass spectroscopy.^{7,8} Also, recently, Glemser, *et al.*, have reported a preparation of S_2F_2 but do not discuss which isomer or the structure.⁹

It is now possible to report for the first time the microwave spectrum of the $FS^{32}S^{34}F$ species and the detailed structural parameters of this isomer. This paper also includes the mass spectrum of FSSF, the dipole moments of both isomers, and other important details omitted in our previous communications.^{5,6} Some of the results in our earlier reports are also repeated here for completeness and to facilitate comparisons between the two isomers.

Experimental

Synthesis.—The isomers of S_2F_2 were prepared by heating *in vacuo* to about the melting point of sulfur (120°) a mixture of dry silver(I) fluoride and sulfur in a glass vessel.¹⁰ Volatile products began to evolve from as low as 100° ; these were condensed by liquid nitrogen as soon as prepared.

Analysis of the products by mass and microwave spectroscopy showed that SO_2 , SF_4 , SOF_2 , SiF_4 , and both isomers of S_2F_2 were produced in varying amounts depending on the reaction conditions.¹¹ The quantities of SO_2 , SOF_2 , and SiF_4 could be reduced by sufficient purification and drying of the AgF . Some selective synthesis of the isomers was also possible since larger proportions of $S=SF_2$ resulted at reaction temperatures above the melting point of sulfur, while FSSF was favored at temperatures just below this.

In the investigation, nearly pure $S=SF_2$ was isolated by low temperature, low pressure fractional distillation using a glass and copper still.¹² This compound and SO_2 were the least volatile products to distil. The FSSF species, however, was studied as a component in the reaction mixtures. This is readily possible for both mass and microwave spectroscopy under favorable circumstances. In this case the reactivity of the FSSF species, evidenced by a characteristic decay in the intensity of its microwave lines, labeled the transitions arising from this species. The other compounds in the mixture did not react in the absorption cell. The growth in intensity of SO_2 and SOF_2 lines indicated that FSSF was being oxidized in the spectrometer.

The Mass Spectrum.—The mass spectra of $S=SF_2$ and a semi-quantitative description for FSSF have been previously reported.^{5,6} It is now possible to evaluate more quantitatively the cracking pattern for FSSF by accounting for the other compounds in the mixtures studied. The contributions of $S=SF_2$, SOF_2 , and SF_4 to mass peaks also arising from FSSF were estimated from their characteristic cracking patterns using a mass peak unique to the compound for calibration. In the case of $S=SF_2$, the unique mass peak was assumed to be the SF_2^+ fragment after accounting for SF_4 and SOF_2 .

After such corrections, a residual, essentially invariant cracking pattern was obtained indicative of a single compound. This cracking pattern, assigned to FSSF, is listed in Table I. The expected isotope ratios were also observed. Actually a small

(5) R. Kuczkowski and E. B. Wilson, Jr., *J. Am. Chem. Soc.*, **85**, 2028 (1963).

(6) R. Kuczkowski, *ibid.*, **85**, 3047 (1963).

(7) F. Seel and D. Gölitz, *Chimia*, **17**, 207 (1963); *Z. anorg. allgem. Chem.*, **327**, 32 (1964).

(8) F. Seel and R. Budenz, *Chimia*, **17**, 335 (1963).

(9) O. Glemser, W. D. Heussner, and A. Haas, *Naturwissenschaften*, **50**, 402 (1963).

(10) M. Centnerswer and C. Strenk, *Ber.*, **56**, 2249 (1923).

(11) A small mass peak at 80 m/e units indicated that SO_2 or SiO was also prepared at times. A simultaneous slight orange coloring of the products favored the presence of SiO . Another likely product is SF_2 . Although the mass spectrum occasionally hinted of its presence, nothing reproducible has as yet been obtained. See, however, ref. 8 and 9.

(12) W. Kirchhoff, Thesis, Department of Chemistry, Harvard University, 1963.

variability ($<10\%$) was seen for different runs. This could be accounted for since the 70 (SF_2^+) mass peak was frequently small and difficult to estimate accurately. The cracking pattern for $S=SF_2$ is also listed in Table I for comparison.

TABLE I

RELATIVE MASS SPECTRAL CRACKING PATTERNS FOR $S_2F_2^a$

m/e	FSSF rel. ^b abundance	$S=SF_2$ rel. abundance	Assignment
102	100	100	$S_2F_2^+$
83	61	30.2	S_2F^+
70	0 ^c	7.4	SF_2^+
64	30	23.2	S_2^+
51	19	6.6	SF^+ ($S_2F_2^{+2}$)
32		26.6	S^+ (S_2^{+2})
19		2.6	F^+
41.5		~ 0.6	S_2F^{+2}
35		<0.1	SF_2^{+2}

^a Obtained with a Consolidated Engineering Corporation spectrometer, Model 21-103C, at 70 ionizing v. and 10- μ a. ionizing current. ^b Peaks below 51 were not measured for this isomer. ^c Assumed.

TABLE II

THE MICROWAVE SPECTRUM OF $S=SF_2$ (Mc.)

Transition	Observed	Calculated
	$S^{32}=S^{32}F_2$	
$3_{12} \rightarrow 3_{22}$	11324.42	11324.85
$0_{00} \rightarrow 1_{10}$	12147.40	12147.27
$1_{11} \rightarrow 2_{12}$	13067.63	(13067.63) ^a
$1_{10} \rightarrow 2_{11}$	14937.61	(14937.61)
$2_{12} \rightarrow 2_{20}$	15577.32	15576.99
$1_{01} \rightarrow 2_{11}$	20083.62	20083.57
$4_{22} \rightarrow 4_{32}$	21911.59	21912.21
$3_{21} \rightarrow 3_{31}$	22796.30	22797.37
$3_{22} \rightarrow 3_{30}$	23486.60	23486.75
$4_{23} \rightarrow 4_{31}$	23915.70	23916.24
$5_{24} \rightarrow 5_{32}$	24843.41	24843.90
$4_{22} \rightarrow 5_{14}$	25012.18	25012.92
$9_{36} \rightarrow 9_{46}$	25804.60	25809.55
$1_{11} \rightarrow 2_{21}$	28505.50	(28505.51)
$2_{02} \rightarrow 3_{12}$	28532.46	28532.05
$2_{11} \rightarrow 3_{21}$	34312.85	34313.12
$4_{32} \rightarrow 5_{33}$	35362.34	35363.16
$2_{12} \rightarrow 3_{22}$	36441.63	36441.81
$3_{03} \rightarrow 4_{13}$	37620.02	37619.81
	$S^{32}=S^{34}F_2$	
$0_{00} \rightarrow 1_{10}$	12068.54	(12068.54)
$1_{01} \rightarrow 2_{11}$	19969.03	(19969.02)
$3_{22} \rightarrow 3_{30}$	23230.90	(23230.90)
$4_{23} \rightarrow 4_{31}$	23651 ± 1	23650.45
$5_{24} \rightarrow 5_{32}$	24554.98	24556.46
$1_{11} \rightarrow 2_{21}$	28304.60	28305.14
$2_{02} \rightarrow 3_{12}$	28371.20	28372.90
$2_{11} \rightarrow 3_{21}$	34109.39	34108.86
$2_{12} \rightarrow 3_{22}$	36205.45	36205.62
	$S^{34}=S^{32}F_2$	
$0_{00} \rightarrow 1_{10}$	12007.65	(12007.65)
$1_{01} \rightarrow 2_{11}$	19676.66	(19676.66)
$4_{22} \rightarrow 5_{14}$	23625 ± 1	23628.00
$3_{22} \rightarrow 3_{30}$	23972.04	(23972.03)
$4_{23} \rightarrow 4_{31}$	24341.36	24340.96
$2_{02} \rightarrow 3_{12}$	27821 ± 1	27824.45
$1_{11} \rightarrow 2_{21}$	28353.30	28353.95

^a Transitions in parentheses used to calculate rotational constants.

The invariant cracking pattern for FSSF supports the assumption that the SF_2^+ fragment is present for $S=SF_2$ but absent or small for FSSF. This is of structural interest since this fragment would not be expected for FSSF except by rearrangement. Therefore, the fragments observed for the two structures are in conformity with those expected by ordinary bond breaking.

TABLE III
 ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA FOR S=SF₂^a

	S ³² =S ³² F ₂	S ³² =S ³⁴ F ₂	S ³⁴ =S ³² F ₂
A	8179.12 ± 0.1 Mc.	8118.30 ± 0.2 Mc.	8173.15 ± 0.2 Mc.
B	3968.15 ± 0.1	3950.24 ± 0.1	3834.50 ± 0.1
C	3033.16 ± 0.1	3030.90 ± 0.2	2955.48 ± 0.2
I _A	61.8075 ± 0.0008 Amu. Å. ²	62.2705 ± 0.0015 Amu. Å. ²	61.8527 ± 0.0015 Amu. Å. ²
I _B	127.3971 ± 0.0033	127.9748 ± 0.0032	131.8375 ± 0.0035
I _C	166.6681 ± 0.0055	166.7924 ± 0.0110	171.0487 ± 0.0116
I _A + I _C - I _B	101.0785 ± 0.0096	101.0881 ± 0.0157	101.0639 ± 0.0166

^a Conversion factor 505,531 Mc. Amu. Å.². The values of I_C and I_C + I_A - I_B for the S³⁴ species were listed incorrectly in the previous communication.⁵

The relative cracking patterns are significantly different which permits the quantities of both isomers in a mixture to be estimated. The ratio of the S₂F⁺-S₂F₂⁺ peaks is particularly useful since it varies between 0.3 to 0.6 for mixtures of the two isomers.

The Microwave Spectrum of S=SF₂.—A conventional Stark modulation spectrometer was used in these studies.¹³ Frequencies were reproducible to 0.1 Mc. Relative intensities were measured with the technique of Esbitt and Wilson with oscilloscope display employed for comparisons on FSSF.¹⁴ The absorption cell was normally at Dry Ice temperature. The temperature dependence studies were made at room and Dry Ice temperatures.

The observed and calculated spectra for three S=SF₂ isotopic species are listed in Table II. Both *a* and *c* dipole transitions were observed for the main isotopic species. Only the more intense *c* dipole transitions were observed for S³²=S³⁴F₂ and S³⁴=S³²F₂. The rotational constants and derived moments of inertia are listed in Table III.

The assignment for these species was made in the usual manner. The near identity of I_A + I_C - I_B for the three species, which indicates that the sulfur *b* coordinates are zero, further confirmed the assignment since S=SF₂ has a symmetry plane containing these atoms. Two sets of vibrational satellites were also observed although not extensively assigned. At Dry Ice temperature they were approximately 4 and 10% the intensity of the main line. These relative intensities compare well with the two lowest vibrational frequencies observed in the infrared spectrum.⁷

The Structure of S=SF₂.—The detailed structural parameters were calculated by the usual procedure of first obtaining the coordinates of the atoms. The sulfur *a* and *c* coordinates were calculated from Kraitchman's equations.¹⁵ The remaining fluorine coordinates were calculated from first and second moment equations. These gave structural parameters of *d*(SS) = 1.860 ± 0.015 Å., *d*(SF) = 1.598 ± 0.012 Å., ∠SSF = 107.5 ± 1°, and ∠FSF = 92.5 ± 1°. The limits of error are sufficient to cover the uncertainty in the rotational constants and also deviations obtained by calculating the structure in different ways from that described above. (The uncertainty in the molecular parameters covers a smaller range than quoted in the earlier communication⁵ because the uncertainty in the S³⁴ C-rotational constants had been estimated larger than necessary.) A projection of the molecule in the *ac* symmetry plane is shown in Fig. 1. Because of the symmetry plane and because data for three isotopic species are available, Fig. 1 illustrates the only way the atoms can be distributed in the four quadrants defined by the *a* and *c* principal axes.

Dipole Moment of S=SF₂.—The dipole moment was obtained by measuring the frequency shifts for S=SF₂ and OCS at the same Stark modulation field. The 3₁₂ → 3₂₂, *M* = 3 component, and 0₀₀ → 1₁₀ transitions of S=SF₂ were compared to the 0 → 1 of OCS. This gave Stark coefficients of 3.70 ± 0.06 × 10⁻⁶ and 1.09 ± 0.02 × 10⁻⁶ Mc./(v.²/cm.²), respectively. The dipole moment was calculated to be μ_a = 0.33, μ_c = 0.97, and μ_T = 1.03 ± 0.03 D. with μ_T and the *c* principal axis forming an angle of 18°44'. Because of the greater electronegativity of fluorine, it is most probable that the negative end of the dipole moment is oriented roughly in the direction of the bisector of the S-F bonds as illustrated in Fig. 1. This orientation is further supported by a prediction of μ_a and μ_c based on bond moment arguments using the microwave data of SO₂,¹⁶

S₂O,¹⁷ and SOF₂¹⁸ and assuming that the center sulfur atom is positive in all cases.

The Microwave Spectrum of FSSF.—The assigned and calculated transitions for the FS³²S³²F and FS³²S³⁴F isotopic species are listed in Table IV. The rotational constants and derived moments of inertia are listed in Table V. The assignment for the main isotopic species was made on the basis of the Stark effect, the agreement with the calculated spectrum, and the characteristic decay in intensity due to decomposition in the absorption cell. In addition, relative intensities and the temperature dependence confirmed the assignment for the less abundant FS³²S³⁴F species. Furthermore, with the relations, (I_A + I_C - I_B) = 4M_Sb_S² + 4M_Fb_F² and M_Sb_S + M_Fb_F = 0 which are valid for the FSSF model, it was possible to calculate the sulfur *b* coordinate using normal isotopic species data alone. The value 0.417 Å. obtained compares well to 0.416 Å. obtained from the Kraitchman method,¹⁵ providing an additional check on the assignment.

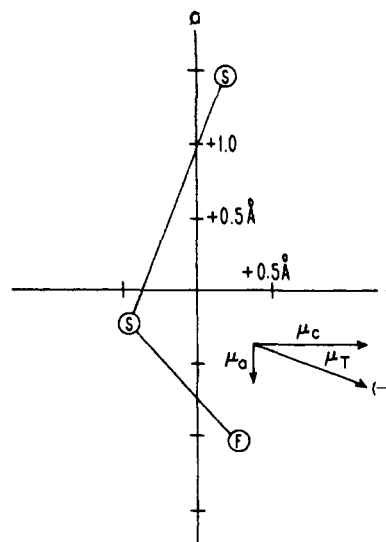


Fig. 1.—Projection of S=SF₂ on symmetry (*ac*) plane; in the actual molecule, the two fluorine atoms would lie above and below the plane and ∠FSF = 92.5 ± 1°, ∠SSF = 107.5 ± 1°, *d*(SF) = 1.598 ± 0.012 Å., and *d*(SS) = 1.860 ± 0.015 Å.

The relative intensity measurements demonstrated interesting and expected effects due to nuclear spin statistical weight factors. First, a 3 to 1 alternation in intensity was observed for rotational levels of opposite symmetry for the normal isotopic species. The intensity alternation was absent for the FS³²S³⁴F species. This is because FSSF possesses a C₂ symmetry axis except for the unsymmetrical isotopic species. When the C₂ axis is present, rotational levels of opposite symmetry have different nuclear spin statistical weight factors. Secondly, after accounting for the spin statistics and the other intensity factors, the transitions from FS³²S³⁴F were about 8% the intensity of the main isotopic species, roughly twice the natural abundance of the sulfur-34 isotope. This is because there are two indistinguishable sites for the sulfur-34 atom in the FSSF molecule.

The Structure of FSSF.—The detailed structural parameters were calculated from the coordinates of the atoms. The three

(13) K. B. McAfee, R. H. Hughes, and E. B. Wilson, Jr., *Rev. Sci. Instr.*, **20**, 821 (1949).

(14) A. Esbitt and E. B. Wilson, Jr., *ibid.*, **34**, 901 (1963).

(15) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).

(16) M. H. Sirvetz, *J. Chem. Phys.*, **19**, 938 (1951).

(17) D. J. Meschi and R. J. Myers, *J. Mol. Spectry.*, **3**, 405 (1959).

(18) R. C. Ferguson, *J. Am. Chem. Soc.*, **76**, 850 (1954).

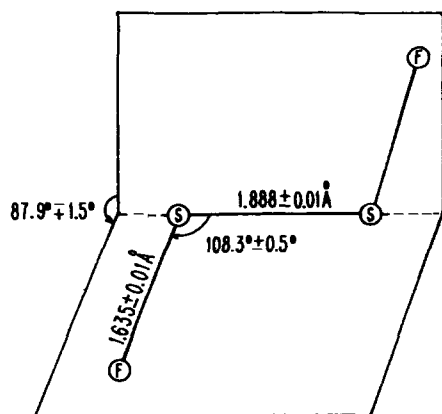


Fig. 2.—The structure of FSSF.

sulfur coordinates were obtained from Kraitchman's equations¹⁵ because of the C_2^b symmetry axis, the two sulfur atoms (or fluorines) must have a and c coordinates differing only in sign. The fluorine a and c coordinates were obtained from second moment equations and the fluorine b coordinates from the first moment condition.

The structural parameters derived from these coordinates are $d(SS) = 1.888 \pm 0.01 \text{ \AA}$, $d(SF) = 1.635 \pm 0.01 \text{ \AA}$, $\angle FSS = 108.3 \pm 0.5^\circ$, and the dihedral angle $= 87.9 \pm 1.5^\circ$. The esti-

mated errors are uncertainties arising from the determination of the rotational constants alone. Since only two isotopic species were studied, estimates were not made on how the structural parameters varied upon calculating them by another method. This structure is illustrated in Fig. 2.

Dipole Moment.—The dipole moment of FSSF was measured by the same method used for $S=SF_2$. The $1 \rightarrow 2M = 0$ lobe of OCS was directly compared to the $2_{02} \rightarrow 3_{12} M = 1$ lobe of FSSF. This gave a Stark coefficient of $2.37 \pm 0.03 \times 10^{-6} \text{ Mc.}/(v^2/\text{cm}^2)$. The dipole moment was calculated to be $1.45 \pm 0.02 \text{ D}$, and lies along the C_2^b symmetry axis. It is most probable that the negative end is directed toward the fluorine atoms.

Discussion

Before discussing the detailed structural parameters, it should be pointed out that the discovery of isomerism in S_2F_2 is the first known case in a S_2R_2 compound. This is because the type of bond exhibited in $S=SF_2$, viz., one which sulfur forms only one bond to sulfur and none to another atom, is rare. The only other known examples are in $S=SO$,¹⁷ $S=SO_3^{-2}$,¹⁹ $S=SO_2R^-$,²⁰ and as terminal atoms in polysulfide ions. On the other hand, the di-, tri-, and polysulfide chain $(-S)_x$ is the usual arrangement of two or more sulfur atoms.

$S=SF_2$.—Aside from the exception noted above, the structural parameters of this species are essentially normal when compared to other molecules. In fact the structure is very similar to the well-known SOF_2 in which $d(SF) = 1.585 \text{ \AA}$, $\angle FSF = 92.8^\circ$, and $\angle FSO = 106.8^\circ$.¹⁸ The SO bond in SOF_2 has been shown to be a double bond experimentally and theoretically.^{18,21} The same result is evident in $S=SF_2$ where the short $d(SS)$ is close to the 1.889 \AA seen in S_2^{22} and $1.884 \pm 0.01 \text{ \AA}$ in $S=SO$.¹⁷

FSSF.—The bond lengths in this molecule are distinctly unusual. The $d(SS)$ and $d(SF)$ are very short and long, respectively, implying that they are not simple covalent single bonds. Typical SS single bonds are 2.05 ± 0.02 and $2.04 \pm 0.03 \text{ \AA}$ observed in HSSH and CH_3SSCH_3 ²³ while the double bond distance of 1.889 \AA is obtained from S_2 . It is striking that the $d(SS)$ in FSSF is almost identical with that in S_2 . Also noteworthy, the $d(SS)$ for S_2Cl_2 and S_2Br_2 , 1.97 ± 0.03 and $1.98 \pm 0.03 \text{ \AA}$, lie approximately between the typical double and single bond distances.²⁴ (The infrared spectrum of FSSF also indicates that the SS bond has definite double bond character and therefore should be distinctly shorter than in $ClSSCl$.²⁵) In contrast the $d(SF)$ in FSSF is long compared to the $1.58 \pm 0.03 \text{ \AA}$ in SF_6 ²⁶ or that in SSF_2 or SOF_2 cited above. In fact, all known SF bond lengths are about 1.60 \AA or shorter except for the axial bond in SF_4 ($1.646 \pm 0.003 \text{ \AA}$)²⁷ and for NSF ($1.646 \pm 0.01 \text{ \AA}$).²⁸

A similar effect on the bonds has been observed in $FOOF$.⁴ In this molecule, the $d(OO)$ is very short and close to that in O_2 , while the $d(FO)$ is comparatively long. The dihedral angle and $\angle FOO$ are also very close to those in FSSF.

TABLE IV
THE MICROWAVE SPECTRUM OF FSSF (Mc.)

Transition	Observed	Calculated
FS ³² S ³² F		
$0_{00} \rightarrow 1_{11}$	13843.46	13843.37
$1_{01} \rightarrow 2_{12}$	18983.41	(18983.41) ^a
$7_{16} \rightarrow 7_{25}$	23368.35	23367.90
$6_{15} \rightarrow 6_{24}$	23871.05	23870.69
$2_{02} \rightarrow 3_{13}$	24018.83	24018.99
$5_{14} \rightarrow 5_{23}$	24355.65	24355.78
$4_{13} \rightarrow 4_{22}$	24798.45	24798.69
$3_{12} \rightarrow 3_{21}$	25178.50	(25178.49)
$7_{17} \rightarrow 7_{26}$	28806.32	28804.42
$3_{03} \rightarrow 4_{14}$	28954.70	28955.09
$8_{18} \rightarrow 8_{27}$	29679.35	29676.97
$1_{10} \rightarrow 2_{21}$	36390.08	(36390.07)
$1_{11} \rightarrow 2_{20}$	36605.47	36605.88
FS ³² S ³⁴ F		
$0_{00} \rightarrow 1_{11}$	13655.84	13655.91
$1_{01} \rightarrow 2_{12}$	18750.31	(18750.31)
$7_{16} \rightarrow 7_{25}$	22988.87	22988.34
$6_{15} \rightarrow 6_{24}$	23482.96	23482.78
$2_{02} \rightarrow 3_{13}$	23741.67	23742.01
$5_{14} \rightarrow 5_{23}$	23959.98	23959.79
$4_{13} \rightarrow 4_{22}$	24395.33	24395.29
$3_{12} \rightarrow 3_{21}$	24768.70	(24768.70)
$7_{17} \rightarrow 7_{26}$	28335.80	28333.54
$3_{03} \rightarrow 4_{14}$	28635.21	28635.90
$1_{10} \rightarrow 2_{21}$	35873.33	(35873.33)

^a Transitions in parentheses used to calculate rotational constants.

TABLE V
ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA FOR FSSF^a

	FS ³² S ³² F	FS ³² S ³⁴ F
A	$11273.35 \pm 0.20 \text{ Mc.}$	$11108.71 \pm 0.20 \text{ Mc.}$
B	2781.92 ± 0.20	2755.53 ± 0.20
C	2570.02 ± 0.10	2547.20 ± 0.10
I_A	$44.8430 \pm 0.0008 \text{ Amu. \AA}^2$	$45.5076 \pm 0.0008 \text{ Amu. \AA}^2$
I_B	181.7202 ± 0.0130	183.4605 ± 0.0133
I_C	196.7031 ± 0.0077	198.4654 ± 0.0076

^a Conversion factor $505,531 \text{ Mc. Amu. \AA}^2$. The rotational constants for the main isotopic species are slightly different from those previously reported⁶ since different transitions were used to calculate them.

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Several explanations for the unusual bond lengths in FSSF can be proposed. First, they could be explained in valence bond theory as arising from a large contribution from the $F-S=S^+F$ ionic structure. Such a structure would be energetically favorable on electronegativity grounds while unfavorable for species like HSSH on similar grounds. This argument is further supported by the $d(SS)$ and $d(SX)$ in CISSCl and BrSSBr which exhibit similar shortening and lengthening but with less drastic effects than in FSSF. A large chemical shift to high fields for the F^{19} n.m.r. absorption also supports this interpretation.²⁵

An alternative explanation for the bond lengths is possible with qualitative molecular orbital theory. This method was first suggested by Professor Lipscomb to account for the short $d(OO)$ and long $d(FO)$ in FOOF.⁴ By analogy, it is also applicable to FSSF. Just as for O_2 , the S_2 molecule is in a $^3\Sigma$ ground state. The two unpaired electrons are in antibonding π -molecular orbitals. A fluorine atom can bond with one of these sulfur electrons giving a resultant three-center bond. This could qualitatively account for the unusual bond lengths and the dihedral angle. The repulsive effect of the fluorine nonbonded electrons is proposed as the reason why this type of bonding is preferred over the normal covalent bonding present in H_2S_2 .

A third way of accounting for the bond lengths is by Linnett's theory of "double quartet formulation of the octet." This method was proposed to explain the structure of FOOF.²⁹ By analogy, it should also be applicable to FSSF although Linnett cautioned against applying it to S_2Cl_2 and S_2Br_2 (and S_2F_2 by inference) on the basis that it is difficult to know whether the number of electrons associated with the sulfur atoms in these molecules should be restricted to eight.

In summary, the S-S and S-F distances in FSSF are anomalously short and long, respectively. They cannot be described as simple covalent single bonds. Simple arguments suffice to show that these unusual bond lengths can be accommodated by the conventional theories of chemical bonds. The arguments are *a posteriori*, nonquantitative, and, particularly in the case of the ionic explanation, not applicable to some other molecules, so that an element of skepticism as to their strength is justified.

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[CONTRIBUTIONS FROM THE DEPARTMENTS OF CHEMISTRY, LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA, AND PURDUE UNIVERSITY, WEST LAFAYETTE, INDIANA]

The Kinetics of the Exchange of Sulfur-35 between Thiosulfate and Sulfide^{1a}

BY ENNIO CIUFFARIN^{1b} AND WILLIAM A. PRYOR^{1c}

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The rate of exchange of sulfur between sodium sulfide-S-35 and sodium thiosulfate has been measured at temperatures between 100 and 140°. The order in sulfide is less than 1, and that in thiosulfate is greater than 1; however, in the presence of added sulfite, the order in both sulfide and thiosulfate becomes 1.0. Using data obtained in the presence of added sulfite, and also data obtained by adding disulfide, the mechanism of the exchange has been concluded to be a displacement on the outer sulfur of thiosulfate by sulfide ion (eq. 2). (Note that sulfide is shown as S^{-2} rather than HS^- in order to simplify the chemical equations.²) However, the mechanism is complicated by a simultaneous exchange of S-35 between disulfide and thiosulfate (eq. 12). Trisulfide and higher polysulfides probably also react in this way, but these reactions are not important in the present system. In addition to these reactions, an exchange occurs between sulfide and disulfide (eq. 5). The rate law for the exchange includes a term in sulfide and one in disulfide (eq. 6). It is shown that this rate law plus the equilibrium reaction (2) explains both the nonintegral kinetic orders in the absence of sulfite and the integral orders produced by the addition of sulfite. The activation energy for k_1 is 17.8 kcal./mole, and the apparent activation energy for the sum of the two terms in eq. 6 is 17.4 kcal./mole. The following values for the rate constants are obtained at 100°, pH 12.46, $\mu = 2.3$, and $(Na^+) 1.5 M$: $k_1 = 9.8 \times 10^{-5}$, $k_2 = 9.5 \times 10^{-3}$, $k_{-1} = 0.13$ (all in $l. mole^{-1} sec^{-1}$).

Introduction

An exchange of radiosulfur is known to occur between sulfide² and thiosulfate ions.

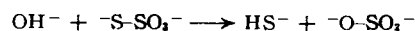


In 1939, in one of the first papers reporting the use of

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(2) In all of the reactions in this paper, sulfide ions will be represented as S^{-2} , although at the pH used the chief sulfide species is HS^- . This simplification eliminates the necessity of writing all the fast acid-base reactions which occur, and it in no way affects the final kinetic equations. The reader, however, should bear the simplification in mind.

sulfur-35, Voge and Libby³ demonstrated that the exchange occurs, and in 1951 Ames and Willard⁴ commented on this exchange on the basis of a few preliminary data. This reaction is an example of a nucleophilic displacement at a noncarbon atom, and such reactions are of considerable current interest. In addition, the reaction bears a formal similarity to the reaction of hydroxide with thiosulfate to produce sulfide and sulfate.



This reaction was reported earlier.^{5,6} It is slower than

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