TABLE I

COMPARISON OF CALCULATED AND OBSERVED DENSITIES, $d^{20}_{4}$

The figures in the first row are calculated from eqs. 10, 12, 13 and 14. Those in the second row are from eq. 11, 15 and 16. The third-row values are observed densities from ref. 4, usually interpolated from data at other temperatures.

| | $m$ | Methyl<br>$p \rightarrow 1$ | Ethyl<br>2 | Propyl<br>3 | Butyl<br>4 | Amyl<br>5 | Hexyl<br>6 | Heptyl<br>7 | Octyl<br>8 |
|---|---|---|---|---|---|---|---|---|---|
| Formate | 1 | | (0.9237) | (0.9043) | (0.8935) | (0.8866) | (0.8816) | (0.8779) | (0.8749) |
| | | (0.9701) | | | | | | | |
| | | .9742 | .9225 | .9057 | | | .8813 | .8784 | .8744 |
| Acetate | 2 | | .9009 | .8883 | .8813 | .8766 | .8733 | .8707 | .8687 |
| | | ( .9330) | | | | | | | |
| | | .9335 | .9007 | .8883 | .8817 | | .8733 | .8707 | |
| Propionate | 3 | | .8904 | .8813 | .8761 | .8725 | .8699 | .8679 | .8662 |
| | | ( .9155) | | | | | | | |
| | | .9152 | .8902 | | | | .8698 | .8679 | .8663 |
| Butyrate | 4 | | .8795 | .8732 | .8696 | .8671 | .8652 | .8638 | .8626 |
| | | .8988 | .8794 | .8733 | .8697 | .8671 | .8652 | .8637 | .8625 |
| | | .8987 | .8792 | | | | .8652 | .8637 | .8629 |
| Valerate | 5 | | .8746 | .8698 | .8670 | .8650 | .8635 | .8623 | .8613 |
| | | .8904 | .8745 | .8699 | .8671 | .8651 | .8635 | .8623 | .8613 |
| Caproate | 6 | | .8713 | .8674 | .8651 | .8635 | .8622 | .8612 | .8604 |
| | | .8845 | .8712 | .8674 | .8652 | .8635 | .8623 | .8613 | .8604 |
| | | .8847 | .8712 | .8675 | .8653 | .8635 | .8622 | .8612 | .8603 |
| Enanthate | 7 | | .8687 | .8656 | .8637 | .8623 | .8612 | .8604 | .8596 |
| | | .8802 | .8686 | .8656 | .8637 | .8623 | .8613 | .8604 | .8597 |
| | | .8801 | .8686 | .8656 | .8638 | .8623 | .8611 | .8604 | .8596 |
| Caprylate | 8 | | .8667 | .8641 | .8625 | .8613 | .8604 | .8596 | .8590 |
| | | .8768 | .8667 | .8641 | .8625 | .8613 | .8604 | .8597 | .8590 |
| | | | .8665 | ( .8659) | .8627 | .8613 | .8603 | .8596 | .8592 |
| Pelargonate | 9 | | .8651 | .8629 | .8615 | .8605 | .8597 | .8590 | .8585 |
| | | .8742 | .8651 | .8629 | .8615 | .8605 | .8597 | .8590 | .8585 |
| | | | .8651 | | | | | | |
| Caproate | 10 | | .8637 | .8618 | .8606 | .8598 | .8591 | .8585 | .8580 |
| | | .8720 | .8638 | .8619 | .8607 | .8598 | .8591 | .8585 | .8580 |

such that the high density values are for the compounds in which the end carbon atom is on the same side of the zigzag axis as the C=O, in the extended zigzag chain.

It would be interesting to look for corresponding regularities and irregularities in amides, ethers, secondary amines, etc., but the data in the literature which could be used for this purpose are very meager.

ROCHESTER, NEW YORK

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

# The Microwave Spectrum, Structure, and Dipole Moment of Thionyl Fluoride[1]

BY RAYMOND C. FERGUSON

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The microwave spectrum of thionyl fluoride, $SOF_2$, from 16,900 to 36,000 mc. has been recorded, and approximately thirty pure rotational transitions identified. The reciprocal moments of inertia fitting the $S^{32}O^{16}F^{19}_2$ spectrum are $a$ = 8614.75 mc., $b$ = 8356.98 mc., $c$ = 4952.96 mc.; and those for the $S^{32}O^{18}F^{19}_2$ spectrum are $a$ = 8582.33 mc., $b$ = 7843.37 mc., $c$ = 4777.90 mc. The structural parameters fitting these moments are: $r_{SO} = 1.412 \pm 0.001$ Å., $r_{SF} = 1.585 \pm 0.001$ Å., $\angle FSF = 92°49' \pm 5'$, $\angle OSF = 106°49' \pm 5'$. Stark effect measurements give a dipole moment of 1.618 ± 0.010 debye units along an axis 38°50′ ± 30′ from the SO bond and 80°23′ ± 30′ from the SF bond.

The closely related compounds thionyl fluoride, $SOF_2$, and sulfuryl fluoride, $SO_2F_2$, are ideal for the study of the effect of strongly electronegative substituents on the adjacent sulfur–oxygen bond. The analysis of the microwave spectrum of sulfuryl fluoride gave structural parameters which definitely disagreed with the electron diffraction results,[2] the most noteworthy feature of the microwave structure being an unusually short S–O bond distance. The present work was undertaken to determine whether a shortening of the S–O bond would be observed in thionyl fluoride. This compound has also been studied by the electron diffraction method, but the results have not been reported in full.[3]

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(1) This work was supported by the Navy Department through the ONR under Task Order V of Contract N5ori-76.

(2) R. M. Fristrom, *J. Chem. Phys.*, **20**, 1 (1952).

(3) D. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, p 307.

## Experimental

**Preparation of Thionyl Fluoride.**—The $S^{32}O^{16}F^{19}_2$ sample was prepared by treating thionyl chloride with antimony trifluoride in the presence of antimony pentachloride.[4] The product was purified by shaking over mercury and by repeated distillation until the vapor pressure and the infrared spectrum showed no further change.

The $S^{32}O^{18}F^{19}_2$ sample was prepared from an oxygen sample enriched to about 23 atom per cent. in the $O^{18}$ isotope.[5] A small volume of this oxygen was heated over an excess of sublimed sulfur and the resulting sulfur dioxide was converted to thionyl fluoride by reaction with argentous fluoride at 200°. Due to the small volume of sample, no extensive purification of the product was undertaken. The only impurities present in more than trace amounts, as indicated by the infrared spectrum, were unreacted sulfur dioxide and some silicon tetrafluoride formed by the reaction of argentous fluoride with the glass system. Silicon tetrafluoride does not absorb in the microwave region, and sulfur dioxide was known to have no absorption lines in the region of particular interest for this work.

**Observed Spectrum.**—A Stark modulation microwave spectrograph[6] was employed to measure the absorption lines of the gas between 16,900 and 36,000 megacycles/second. All frequencies were measured with a crystal-driven frequency standard calibrated against the 5-mc. signal from station WWV. The frequencies reported are believed to be accurate to 0.1 mc.

Approximately 130 absorption lines were observed in the region of the spectrum covered. Quantitative measurements of the Stark effects of several lines were made for identification purposes and for dipole moment calculations.

The zero-based square wave generator and the wave guide were calibrated by measuring the Stark lobes of the $J = 1 \rightarrow 2$ transition of $O^{16}C^{12}S^{32}$ in the ground vibrational state and using the dipole moment given by Shulman and Townes[7] for the calculation of the electric field strengths.

## Analysis of Spectrum

**$S^{32}O^{16}F^{19}_2$ Transitions.**—The analysis was aided by a rough prediction of the spectrum from the electron diffraction data. Since the molecule is pyramidal and asymmetric, the dipole moment is not constrained to lie along a principal axis, and transitions associated with its components along the two axes in the symmetry plane may occur.

Three $J = 1 \rightarrow 2$ pure rotational transitions near 34,000 mc. were identified by means of their Stark effects and were assigned as the $\Delta K_{-1} = 1$, $\Delta K_1 = 0$ type.[8] Three other lines at somewhat lower frequencies were identified as the type $J = 1 \rightarrow 2$, $\Delta K_{-1} = 0$, $\Delta K_1 = 1$. The latter transitions were considerably weaker, and a detailed study of their Stark patterns was hindered by the presence of several stronger lines. However, the Stark effects observed for these lines were qualitatively correct. The identifications were confirmed when the assignment of three of the lines yielded reciprocal moments of inertia which correctly predicted some twenty-odd additional pure rotational transitions (Table I).

TABLE I

IDENTIFIED PURE ROTATIONAL TRANSITIONS OF THIONYL FLUORIDE

| Transition | Frequency, mc./sec. | $\nu_{obsd.} - \nu_{calcd.}$, mc./sec. | Relative intensity (calcd.) |
|---|---|---|---|
| | $S^{32}O^{16}F^{19}_2$ Transitions | | |
| $0_{00} \rightarrow 1_{10}$ | 16,971.79 | 0.06 | 1.00 |
| $1_{01} \rightarrow 2_{11}$ | 33,685.69 | [a] | 1.50 |
| $1_{10} \rightarrow 2_{20}$ | 33,957.43 | −0.12 | 1.99 |
| $1_{11} \rightarrow 2_{21}$ | 34,201.22 | [a] | 1.50 |
| $1_{11} \rightarrow 2_{12}$ | 23,216.06 | 0.20 | 0.17 |
| $1_{01} \rightarrow 2_{02}$ | 23,459.49 | −0.04 | .23 |
| $1_{10} \rightarrow 2_{11}$ | 30,023.90 | [a] | .17 |
| $2_{12} \rightarrow 3_{13}$ | 33,242.36 | 0.28 | .30 |
| $2_{02} \rightarrow 3_{03}$ | 33,255.43 | −0.26 | .34 |
| $4_{23} \rightarrow 4_{22}$ | 17,500.91 | −1.34 | 0.19 |
| $5_{33} \rightarrow 5_{32}$ | 17,304.89 | −2.42 | .36 |
| $6_{43} \rightarrow 6_{42}$ | 16,980.58 | −2.54 | .53 |
| $4_{14} \rightarrow 4_{13}$ | 24,703.35 | 0.80 | .05 |
| $5_{24} \rightarrow 5_{23}$ | 24,682.55 | 2.31 | .15 |
| $6_{34} \rightarrow 6_{33}$ | 24,642.79 | 6.13 | .29 |
| $7_{44} \rightarrow 7_{43}$ | 24,553.93 | −3.93 | .45 |
| $8_{54} \rightarrow 8_{53}$ | 24,419.36 | −6.07 | .61 |
| $9_{64} \rightarrow 9_{63}$ | 24,205.50 | −6.94 | .77 |
| $10_{74} \rightarrow 10_{73}$ | 23,879.57 | −9.24 | .93 |
| $11_{84} \rightarrow 11_{83}$ | 23,409.65 | −10.73 | 1.09 |
| $12_{94} \rightarrow 12_{93}$ | 22,765.11 | −11.44 | 1.25 |
| $13_{10,4} \rightarrow 13_{10,3}$ | 21,924.71 | −11.33 | 1.40 |
| $14_{11,4} \rightarrow 14_{11,3}$ | 20,881.41 | −10.00 | 1.55 |
| | $S^{32}O^{18}F^{19}_2$ Transitions | | |
| $1_{01} \rightarrow 2_{11}$ | 32,112.44 | [a] | 0.45 |
| $1_{10} \rightarrow 2_{20}$ | 32,969.48 | [a] | .60 |
| $1_{11} \rightarrow 2_{21}$ | 33,590.51 | [a] | .45 |

[a] Assigned for calculation of reciprocal moments of inertia.

**$S^{31}O^{18}F^{19}_2$ Transitions.**—Although the natural abundance of $S^{34}$ is about 4%, none of the observed lines could be identified as arising from the $S^{34}O^{16}F^{19}_2$ species. In order to determine the structure of thionyl fluoride, it was necessary to prepare an isotopic sample. The $O^{18}$ isotope was chosen because substitution far from the molecule's center of mass was to be preferred.

Estimates of the frequencies of the $S^{32}O^{18}F^{19}_2$ transitions could be made from the spectrum of the normal isotopic species. The three stronger $J = 1 \rightarrow 2$ transitions were readily found and identified by a detailed study of their Stark effects. The moments of inertia for the new isotopic species were calculated and found to be consistent with the moments for the normal species (Table II).

TABLE II

RECIPROCAL MOMENTS OF INERTIA FOR THIONYL FLUORIDE (MC./SEC.)

| Reciprocal moment | $S^{32}O^{16}F^{19}_2$ | $S^{32}O^{18}F^{19}_2$ |
|---|---|---|
| $a$ | 8614.75 ± 0.10 | 8582.33 ± 0.10 |
| $b$ | 8356.98 ± .10 | 7843.37 ± .10 |
| $c$ | 4952.96 ± .10 | 4777.90 ± .20 |
| $K = \dfrac{2b - a - c}{a - c}$ | 0.859213 | 0.611526 |

After the molecular structure had been determined as described below, the final model was used to predict the stronger $J = 1 \rightarrow 2$ transitions of $S^{34}O^{16}F^{19}_2$. An estimate placed their intensities near the lower limit of sensitivity of the spectro-

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(4) This sample was prepared by Dr. J. K. O'Loane, who kindly furnished a portion of his product for the microwave study.

(5) The oxygen sample was furnished by Prof. Alfred O. C. Nier of the University of Minnesota, where the isotopic separation was made possible by a grant from the American Cancer Society acting through the Committee on Growth of the National Research Council.

(6) K. B. McAfee, R. H. Hughes and E. B. Wilson, Jr., *Rev. Sci. Instruments*, **20**, 621 (1949).

(7) R. Shulman and C. H. Townes, *Phys. Rev.*, **77**, 500 (1950).

(8) The notation of G. W. King, R. M. Hainer and P. C. Cross, *J. Chem. Phys.*, **11**, **27** (1943), is used.

graph. The lines were apparently too weak to be observed under the conditions used, for none of them were found.

## Structural Parameters

The observed microwave spectrum is consistent with the pyramidal structure assigned by the electron diffraction work, except that the identification of two of the principal axes must be changed. The two types of transitions observed require the *a*- and *c*-axes, *i.e.*, the axes having the least and greatest moments of inertia, to lie in the symmetry plane of the molecule. The electron diffraction model placed the *b*- and *c*-axes in the symmetry plane; the interchange of the *a*- and *b*-axes indicates that the angles reported are too large.

The frequencies of the transitions which would occur if the dipole moment had a non-zero component along the intermediate axis were calculated, but none of these transitions were observed. The absence of such transitions indicates that the *b*-component of the dipole moment must be small or zero, and this tends to support the assumption that the two S–F distances are equal.

A more rigorous test of the moments of inertia and the identification of the symmetry plane is possible because the moment of inertia about that plane should be unchanged by isotopic substitution in the plane. Assuming the effect of zero-point vibration to be negligible, the moment about the symmetry plane is due to the fluorine atoms only, and

$$2Fz_F^2 = (1/2)(I_c + I_a - I_b) \qquad (1)$$

where $F$ is the mass and $z_F$ is the coördinate of fluorine along the *b*-axis, and the $I$'s are the principal moments of inertia. The observed moments defined by (1) are identical, within experimental error, for both isotopic species of thionyl fluoride. The F–F distance was obtained by use of this relationship.

The three remaining molecular parameters were calculated by fitting the projection in the symmetry plane to the moments about the two planes perpendicular to the symmetry plane, which can be obtained by relations like the right side of (1). Since there are two such independent moments for each isotopic species, the three additional parameters could be obtained, with one moment left for an independent test.

The labor involved in finding the correct model was greatly shortened by the following procedure for obtaining corrections for the parameters of trial models. General formulas for calculating the partial derivatives of the moments of inertia with respect to bond stretching and angle bending have been derived by Kivelson and Wilson.[9] The application of these derivatives through

$$I_c + \sum_i (\partial I/\partial r_i)\Delta r_i \approx I_0 \qquad (2)$$

provides a method of calculating the corrections for the trial parameters. In (2) $I_0$ and $I_c$ are the observed and calculated moments of inertia, $\partial I/\partial r_i$ is the derivative with respect to the *i*th bond distance or angle, and $\Delta r_i$ is the corresponding correction. The application of equation 2 is an approximation process, and there is a tendency to overcorrect; the moments of inertia must be recalculated for each set of corrected parameters until the observed and predicted moments agree.

The above procedure was applied to the thionyl fluoride models until the best fit for all four remaining independent moments was obtained. The difference between the calculated moments for the final model and the observed moments was well within experimental error. Table III summarizes the results and includes the electron diffraction results for comparison.

TABLE III

MOLECULAR PARAMETERS FOR THIONYL FLUORIDE

| Parameter | Microwave | Electron diffraction |
|---|---|---|
| F–F | 2.297 ± 0.001 | |
| S–O | 1.412 ± .001 | 1.45 |
| S–F | 1.585 ± .001 | 1.6 |
| ∠F–S–F | 92°49′ ± 5′ | 106° |
| ∠O–S–F | 106°49′ ± 5′ | 114° |

The physical atomic weights given by Mattauch[10] and the physical constants reported by Dumond and Cohen[11] were used. The relationship between the reciprocal moment and 'the corresponding moment of inertia was $I_a(amu - A^2) = 505{,}424/a$ (mc./sec.).

## Dipole Moment

The frequency shifts of the Stark lobes of several of the transitions were measured as a function of the electric field strengths. The slopes of the lobes which were second order in the field strength were obtained by the method of least squares and are given in Table IV.

TABLE IV

SECOND-ORDER STARK LOBES OF THIONYL FLUORIDE

$\Delta\nu_M$(mc./sec.) = $sE^2$ (e.s.u./cm.)$^2$

| Transition | $M$ | Slope, *s*, in 2nd-order plot | |
|---|---|---|---|
| | | $S^{32}O^{16}F^{19}_2$ | $S^{32}O^{18}F^{19}_2$ |
| $0_{00} \rightarrow 1_{10}$ | 0 | 1.812 | |
| $1_{01} \rightarrow 2_{11}$ | 0 | 0.3101 | 0.2862 |
| $1_{11} \rightarrow 2_{21}$ | 0 | .4164 | .4194 |
| $1_{10} \rightarrow 2_{20}$ | 0 | − .4577 | − .4617 |
| | 1 | .1237 | .1018 |

Limits of error on all lobes ±1%

The components of the dipole moment along the two principal axes in the symmetry plane were calculated by the method of Golden and Wilson.[12] The relationship used was

$$\Delta\nu_M = \{(A_a + B_aM^2)\mu_a^2 + (A_c + B_cM^2)\mu_c^2\}E^2$$

where $\Delta\nu_M$ is the frequency shift for the lobe having magnetic quantum number $M$, $A$ and $B$ are the reduced Stark coefficients calculated by Golden and Wilson, $\mu$ is the dipole moment component along a principal axis, the subscripts indicate the axis in question, and $E$ is the electric field strength. Linear interpolation in the tables of reduced Stark coefficients was used, except that Lagrangian interpolation coefficients were applied wherever

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[9] D. Kivelson and E. B. Wilson, Jr., *J. Chem. Phys.*, **21**, 1229 (1953).

[10] J. Mattauch, *Rev. Mod. Phys.*, **9**, 245 (1937).

[11] J. W. M. Dumond and E. R. Cohen, *ibid.*, **20**, 82 (1948).

[12] S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

necessary to make the interpolation accurate to ±0.5%. The dipole moment components were calculated from pairs of simultaneous equations and then were averaged to obtain the best fit for all measured second-order Stark lobes (Table V).

TABLE V

DIPOLE MOMENTS FOR THIONYL FLUORIDE

| Moment or angle, $\mu$ | $S^{32}O^{16}F^{19}{}_2$, $D$ | $S^{32}O^{18}F^{19}{}_2$, $D$ |
|---|---|---|
| $\mu$ | 1.618 ± 0.010 | 1.618 ± 0.010 |
| $\gamma$ | 18°40′ ± 15′ | 20°48′ ± 45′ |
| $\alpha$ | 57°47 ′ ± 5′ | 58°56′ ± 5′ |
| $\beta$ | 57° 2′ ± 5′ | 55°52″ ± 5′ |
| $\alpha - \gamma$ | 39° 7′ | 38° 8′ |

Weighted average: $\mu = 1.618 \pm 0.010$ $D$, 38°50′ ± 30′

Near the limiting case of the oblate symmetric rotor, which is the case with thionyl fluoride, the $1_{01}$ level is degenerate with the $1_{11}$ level, and the $2_{11}$ level with the $2_{21}$ level. The degeneracy gives rise to a linear term in the expression for the frequency shift of the $M = 1$ Stark lobes of the lines arising from these levels. These lobes have been calculated for the $S^{32}O^{16}F^{19}{}_2$ and compared with the observed lobes. The good fit obtained in Fig. 1 further confirms the consistency of the assignments and also provides an independent check on the value of the dipole moment.

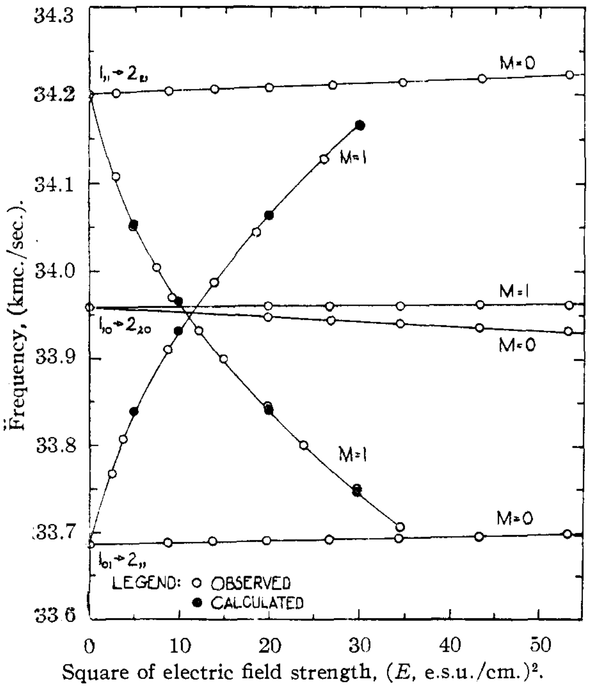
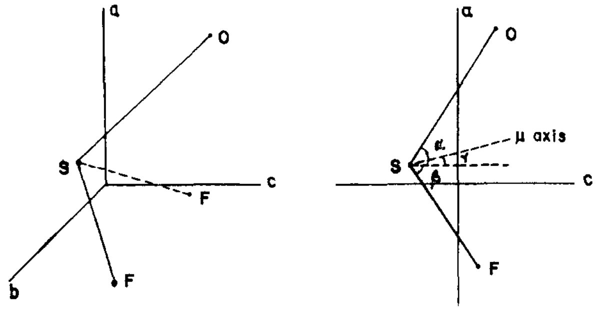


Fig. 1.—Stark effects for $S^{32}O^{16}F_2{}^{19}$, $J = 1 \to 2$.

The orientation (but not the sign) of the axis of the dipole moment can be determined by considering the effect of isotopic substitution on the two components (Table V). The earlier calculation of the moments of inertia showed that substitution of $O^{18}$ increased angle $\alpha$ in Fig. 2b, which is the projection of the molecule on the symmetry plane. Since the $a$-component of the dipole moment also increased in this substitution, the angle between the S–O bond and the dipole moment axis must be that indicated in the figure and in Table V. The orientation should be the same in both isotopic species and the dipole moment is reported as 1.618 ± 0.010 debye units, 38°50′ ± 30′ from the S–O bond and 80°23′ ± 30′ from the S–F bonds. The results have been weighted in favor of the values for the normal isotopic species, since more measurements were made and the standard deviation was smaller. The electronegativities are in the order S < O < F; this indicates that the negative end of the dipole should be directed away from the sulfur atom along the positive $a$- and $c$-axes in Fig. 2.



2a. Perspective. 2b. Symmetry plane.

Fig. 2.—$SOF_2$ in its principal axis system.

## Discussion

The reason for disagreement between the microwave and electron diffraction structures for the molecule is difficult to determine, since no discussion of the other work has been published. In view of the internal consistency of the microwave analysis, and of the apparently tentative nature of the electron diffraction model, the microwave parameters are preferred.

The S–O distance is 0.020 Å. shorter than the microwave value for sulfur dioxide (1.432 Å.) but the value is approximately that expected for a double bond. The S–F distance and ∠FSF are nearer the microwave results for sulfuryl fluoride than is the S–O distance (in $SO_2F_2$ $r_{S-F} = 1.57$ Å., ∠FSF = 92°47′, and $r_{SO} = 1.37$ Å.). In both compounds ∠FSF is near the angle in hydrogen sulfide (92°16′).

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