SULFUR MONOFLUORIDE: THE MICROWAVE SPECTRUM OF A SECOND ISOMER[1]

Sir:

Three recent communications have been published concerning sulfur monofluoride. Kuczkowski and Wilson[2] using mass and microwave spectroscopy showed that one of the reaction products obtained by heating argentous fluoride and sulfur is the pyrimidal $S=SF_2$ form. Seel and Golitz,[3] using a different synthesis, were also able to establish the existence of the pyrimidal $S=SF_2$ form on the basis of its infrared spectrum. Glemser, Heussner and Haas[4] have also reported a preparation of S_2F_2 but have not drawn any conclusions as to the structure. We are now able to demonstrate that a second isomer of S_2F_2 exists with a non-planar chain FSSF structure analogous to S_2Cl_2.[5]

The first indication that two isomeric forms of S_2F_2 existed[6] was obtained during the earlier investigation of the $S=SF_2$ form.[2] When the crude products of the reaction between AgF and S were volatilized at different rates into the mass spectrometer, a varied cracking pattern was obtained for mass peaks attributable to S_2F_2. In addition, with a sample in the microwave cell at dry ice temperature, a set of absorptions was noted whose intensity steadily decreased with a first order half life of approximately 15 minutes. These microwave lines could not be explained by the $S=SF_2$ form or known impurities. Both of these properties disappeared when the reaction products were fractionally distilled in order to obtain pure $S=SF_2$, presumably due to decomposition of the reactive FSSF species with the distillation apparatus.

6 p

In the investigation of the microwave lines from FSSF, it was found possible to enhance their initial intensity by dosing of the bulk reaction product into the absorption cell from slush baths below -100°C. A complete separation was unnecessary since the characteristic decay rate identified the transitions arising from the FSSF species.

The observed and calculated microwave spectra for this species are listed in Table I. The transitions were assigned on the basis of their Stark effects and argreement obtained with the calculated rigid rotor spectrum. The rotational constants used in the calculation and the derived moments of inertia are listed in Table II. An alternation in intensity due to nuclear spin statistical weights was observed for transitions of different symmetry. Rough intensities for the $3_{12} \rightarrow 3_{21}$, and $5_{14} \rightarrow 5_{23}$ transitions compared to the $4_{13} \rightarrow 4_{22}$ transition indicated a nuclear statistical weight factor of 3 to 1 respectively. This establishes that the molecule has a C_2 symmetry axis which can exchange a pair of equivalent fluorine atoms with nuclear spin of $\frac{1}{2}$. Quantitative measurements of the frequency shifts vs voltage squared for the three Stark lobes of the $2_{02} \rightarrow 3_{13}$ transitions indicated that only "b" type selection rules were operating which further confirms the C_2 axis.

It proved possible to correlate the intensity of the microwave lines with mass spectral peaks. Whenever the microwave lines reported here were absent from a sample, the mass spectrum could be explained in terms of the $S{=}SF_2$ isomer and/or known impurities. However, when these transitions were intense, then the 51(SF^+),

$64(S_2^+)$, $83(S_2F^+)$ m/e peaks increased while the $70(SF_2^+)$ m/e peak decreased relative to the $102(S_2F_2^+)$ m/e peak when compared to the cracking pattern of pure $S{=}SF_2$. No unexplained peaks were detected to m/e units greater than 102.

The mass spectral data demonstrate that sulfur and fluorine are elements in the molecule giving rise to the microwave spectrum and indicate that it almost certainly has the molecular formula S_2F_2. The nuclear spin statistics and absence of an unpaired electron also permit only two fluorine atoms in the molecule. The moments of inertia alone can eliminate SF_2, and pyrimidal or chain S_3F_2 as possibilities. The only possible species remaining which gives reasonable structural parameters is a non-planar, chain type FSSF molecule. The moments of inertia are insufficient to calculate a unique structure for this species without assuming one parameter. Hence they fit a range of structures with d(SS) between 1.85-2.05 Å, d (SF) between 1.55-1.65 Å and ∠SSF and dihedral angles in the vicinity of 109° and 90° respectively. This type of structure is similar to that reported for S_2Cl_2 and S_2Br_2.[5] For example, S_2Cl_2 has d(SS) = 1.97 ± 0.03 Å ∠SSCl = 107° ± 2.5°, and dihedral angle of 82.5° ± 12°.[5] The range of sulfur fluorine bond lengths is also reasonable compared to other molecules.[7,8]

Therefore on the bases of the correlation of the microwave spectrum with mass spectral peaks, the alternating intensities due to fluorine nuclear spin statistical weights and the reasonable structure which will fit the moments of inertia, we conclude that the reported microwave spectrum is due to the non-planar chain

FSSF form of sulfur monofluoride and consequently that S_2F_2 exists in two isomeric forms.

REFERENCES

1. This work was supported by a grant extended Harvard University by the Office of Naval Research.
2. R. Kuczkowski and E. Bright Wilson, Jr.,J. Am. Chem. Soc. 85, 2028 (1963).
3. F. Seel and D. Gölitz, Chimia, 17, 207 (1963).
4. Von O. Glemser, W.-D. Heussner and A. Haas, Naturwissenschaften, 50, 402 (1963).
5. E. Hirota, Bull. Chem. Soc. Japan, 31, 130 (1958).
6. R. Kuczkowski, Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, June, 1963.
7. William Kirchhoff and E. Bright Wilson, Jr., J. Am. Chem. Soc. 84, 334 (1962.) See Table III in paper.
8. W. M. Tolles and W. D. Gwinn, J. Chem. Phys. 36, 1119 (1962).

Mallinckrodt Chemical Laboratory
Harvard University
Cambridge, Massachusetts

Robert L. Kuczkowski

Table I. Microwave Spectrum of FSSF[a]

Transition	Observed	Calculated
$0 \to 1_{11}$	13843.46	13843.47
$1_{01} \to 2_{12}$	18983.41	(18983.41)[b]
$7_{16} \to 7_{25}$	23368.35	23366.31
$6_{15} \to 6_{24}$	23871.05	23869.35
$2_{02} \to 3_{13}$	24018.83	(24018.83)
$5_{14} \to 5_{23}$	24355.65	24354.79
$4_{13} \to 4_{22}$	24798.45	24798.05
$3_{12} \to 3_{21}$	24178.50	25178.18
$7_{15} \to 7_{26}$	28806.32	28807.72
$3_{03} \to 4_{14}$	28954.70	(28954.70)
$8_{18} \to 8_{27}$	29679.35	29681.16
$1_{10} \to 2_{21}$	36390.08	36390.47
$1_{11} \to 2_{20}$	36605.47	36606.50

[a] A conventional Stark modulated spectrometer was employed. Frequencies were reproducible to ±0.1 Mc.

[b] Transitions in parenthesis used to calculate the rotational constants.

Table II. Rotational Constants and Moments of Inertia for $F^{32}S^{32}SF$

A	B	C
11273.50 Mc/sec	2782.08 Mc/sec	2569.97 Mc/sec
I_a	I_b	I_c
44.8424 AmuÅ^2	181.7097 AmuÅ^2	196.7069 AmuÅ^2