

Microwave Spectrum and Structure of Sulfur Difluoride

Abstract. Sulfur difluoride has been identified and characterized from its microwave spectrum. The analysis of rotational transitions for both sulfur difluoride-32 and sulfur difluoride-34 shows that this molecular species has C_{2v} symmetry with a bond length of 1.589 angstroms, a bond angle of $98^\circ 16'$, and a dipole moment of 1.05 Debye.

We report the first positive identification of sulfur difluoride (SF_2). Characterization of this species was achieved solely by the application of microwave spectroscopic techniques. This result provides excellent support for the arguments presented by Wilson in a recent review article (1), in which he discussed the importance of microwave spectroscopy as a tool for characterizing new molecules.

Although there have been several attempts to prepare SF_2 , it appears doubtful that its synthesis by conventional chemical methods has been demonstrated. Glemser *et al.* (2) report that SF_2 can be produced by the decomposition of SSF_2 , but Seel (3) disagrees with this result. On the other hand, Padma and Satyanarayana (4) report the production of SF_2 by the thermal decomposition of AgF in the presence of molten sulfur. Kuczkowski (5) has used this same reaction mixture for the production of $FSSF$ and SSF_2 , and he remarks that a possible side product is SF_2 . However, he also points out that the mass spectrum of the gases

Table 1. Microwave spectrum and constants of $^{32}SF_2$. Values for A , B , and C are expressed in megahertz; those for I_A , I_B , and I_C as atomic mass units ($\text{\AA}^2$).

Transition	Observed frequency (Mhz $\pm$ 0.02)*	Calculated frequency (Mhz) (rigid rotor)
$2_{12} \leftarrow 1_{01}$	47,468.04	47,467.13
$4_{02} \leftarrow 3_{13}$	49,356.29	49,356.75
$2_{20} \leftarrow 2_{11}$	53,372.52	53,375.47
$3_{21} \leftarrow 3_{12}$	50,843.68	50,845.68
$4_{22} \leftarrow 4_{13}$	48,531.71	48,531.65
$5_{23} \leftarrow 5_{14}$	47,175.57	47,173.91
$6_{24} \leftarrow 6_{15}$	47,452.06	47,448.99
$7_{25} \leftarrow 7_{16}$	49,896.43	49,893.95
$8_{26} \leftarrow 8_{17}$	54,911.76	54,913.81
$A = 26,929.40 \pm 0.47^\dagger$		$I_A = 18.7725$
$B = 9,211.36 \pm 0.29$		$I_B = 54.8813$
$C = 6,845.91 \pm 0.29$		$I_C = 73.8442$
$I_C - I_A - I_B = 0.1904$		

* This error is an estimate of the accuracy of measurements. $\dagger$ Standard errors from a least-squares fit of the experimental data.

evolved did not conclusively show the presence of SF_2 .

In the microwave range of the electromagnetic spectrum, power absorptions occur generally as a result of a change in the rotational energy of the molecule in question (6). Therefore, the correct interpretation of this spectrum allows the determination, to a high degree of accuracy, of the principal moments of inertia and thus the structure of the molecule.

In this investigation we employed a parallel-plate microwave absorption cell (7) in a fast-flow spectrometer that was designed for the study of transient species (8). Sulfur hexafluoride was passed through a radio frequency discharge and the products reacted with carbonyl sulfide downstream from the discharge zone. The resulting reaction products were then pumped through the parallel-plate absorption cell. While searching these reaction products for absorption signals from the SF radical, several strong absorptions, which appeared to come from a relatively stable, nonparamagnetic molecule, were detected in the 50 Ghz region. Careful inspection of the absorption signals under the effect of an externally applied electric field (Stark effect) allowed definite rotational quantum-number assignments to be made for some of these signals. On the basis of these assignments it was apparent that the carrier of the spectrum was a polyatomic species.

Predictions were made to extend the spectrum under the tentative assumption that the species responsible was $^{32}SF_2$. The subsequent observation of several more absorption signals that could definitely be assigned to the species in question permitted a least-squares fit of the absorption frequencies to standard rigid-rotor formulation. The results of this fit appear in Table 1; good agreement exists between the calculated and observed frequencies. At this point it was possible to eliminate from consideration other species thought to be present in the reaction products. The suspected species SSF_2 , $FSSF$, OF_2 , SiF_2 , COF_2 , SOF_2 , SO_2 , and SF_4 were eliminated by comparing the published values (5, 9-11) of the rotational constants (A , B , C) for these molecules with the observed values given in Table 1.

Careful inspection of the moments of inertia given in Table 1 will provide important structural information. The inertial defect ($I_C - I_A - I_B$) is a small positive number, which is strong evi-

Table 2. Microwave spectrum and constants of $^{34}SF_2$. Values for A , B , and C are expressed in megahertz; those for I_A , I_B , and I_C as atomic mass units ($\text{\AA}^2$).

Transition	Observed frequency (Mhz $\pm$ 0.05)*	Calculated frequency (Mhz) (rigid rotor)
$2_{12} \leftarrow 1_{01}$	46,438.56	46,438.56
$4_{04} \leftarrow 3_{13}$	49,853.29	49,851.15
$5_{23} \leftarrow 5_{14}$	44,982.21	44,983.68
$6_{24} \leftarrow 6_{15}$	45,658.72	45,657.74
$7_{25} \leftarrow 7_{16}$	48,659.53	48,657.86
$8_{26} \leftarrow 8_{17}$	54,380.70	54,381.80
$A = 26,071.56 \pm 0.61^\dagger$		$I_A = 19.3901$
$B = 9,211.42 \pm 0.53$		$I_B = 54.8809$
$C = 6,789.00 \pm 0.49$		$I_C = 74.4632$
$I_C - I_A - I_B = 0.1922$		

* This error is an estimate of the accuracy of measurements. $\dagger$ Standard errors from a least-squares fit of the experimental data.

dence that the molecule in question is planar. In addition, it is hard to rationalize the magnitude of the observed moments of inertia for a molecule with more than three atoms.

The absorption signals listed in Table I have the characteristics of μ_b type transitions, that is, transitions that are active through the component of the permanent dipole moment along the intermediate axis of inertia. Furthermore, accurate measurements of the Stark effect lead to the result

$$\mu_b = 1.05 \text{ Debye}$$

$$\mu_a = 0$$

and the planarity of the molecule requires $\mu_c = 0$. This conclusion that the dipole moment is coincident, to a high degree of accuracy, with the b -axis is a strong indication that this is a two-fold symmetry axis (higher symmetry is precluded because of the observed planarity of the molecule). We are therefore led to the conclusion that the carrier of the spectrum is very probably a molecule of the bent AB_2 type.

The absorption corresponding to the transitions $2_{12} \leftarrow 1_{01}$ and $6_{24} \leftarrow 6_{15}$ occurred sufficiently close together for a direct comparison of their relative intensities. Within the accuracy of measurement, the intensities of the two transitions were equal. However, a relative intensity calculation in the rigid rotor approximation showed that equal intensities could be accounted for only by including effects due to nuclear spin. This required that two atoms of nuclear spin one-half be placed symmetrically off a twofold axis of symmetry. Of the atoms likely to be present in the reaction products, only fluorine has spin one-half.

The arguments presented above have

established that the carrier of the observed microwave spectrum is a triatomic molecule of C_{2v} symmetry with fluorine atoms in the off-axis positions. The identity of the third atom in this molecule can be confirmed from the effects of isotopic substitution. Assuming the molecule in question to be $^{32}\text{SF}_2$ the following structure was obtained from the moments of inertia given in Table 1:

$$r_0(\text{S-F}) = 1.589 \text{ \AA}$$

$$\angle \text{FSF} = 98^\circ 16'$$

The mass 34 isotope of sulfur occurs in 4.22 percent natural abundance which should yield sufficient concentration of a species bearing this isotope to be observable. A new spectrum was calculated for $^{34}\text{SF}_2$ based on the structure determined above. Six transitions were observed very close to the predicted frequencies, thus confirming that the central atom is sulfur. The observed frequencies and constants for the $^{34}\text{SF}_2$ species are given in Table 2. It may be noted that the moment of inertia I_B remains essentially unchanged upon isotopic substitution, as would be expected for an atom on an axis of symmetry.

Questions concerning reactivity and lifetime can be answered only in a qualitative fashion because of the method used to prepare SF_2 . Sulfur difluoride was trapped in the waveguide by simultaneously closing the inlet and outlet valves while it was being synthesized in the discharge. In this static system the microwave signals decreased to half-intensity in about 12 minutes. However, the method of generation appears to produce such a wide variety of other substances of unknown reactivity that this measurement may not be meaningful. On the basis of the relatively long time required for the apparent destruction of SF_2 , it appears that if this substance is prepared in reasonable purity it should be stable enough to permit studies in a static system, especially if reduced temperatures are employed.

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12. Supported by the Division of Research, AEC. We thank Dr. William H. Kirchhoff for his aid with the initial calculations and for helpful discussions throughout the course of this work. F.X.P. is on sabbatical leave from the Catholic University of America. This report is a contribution of the National Bureau of Standards and is not subject to copyright.

14 February 1969

Interhemispheric Transport of Atmospheric Fission Debris from French Nuclear Tests

Abstract. *Radioactive iodine-131 (half-life, 8.06 days) and barium-140 (half-life, 12.8 days), released into the atmosphere (21°S, 137°W) by the French nuclear tests conducted during the period 24 August to 8 September 1968, have been observed in rainfall at Arkadelphia, Arkansas (34°N, 94°W). The maximum time required for the transport of the debris from a mid-southern to a mid-northern latitude appears to be about 3 weeks.*

The study of fission debris from single-event nuclear tests has increased our knowledge of the worldwide transport processes that occur within the atmosphere. Debris injected into the atmosphere halfway around the world (but at approximately the same latitude) can circle the earth several times before the occurrence of complete dis-

persal or washout or both (1). Each cycle about the earth requires about 3 weeks.

The recent nuclear tests conducted by the French provided a unique opportunity to study the possible transport of nuclear debris from a mid-southern to a mid-northern latitude. Samples of rainfall were collected by means of a sampling system installed on the campus of Henderson State College. Gross activities were determined by acidifying a 0.5-liter sample of rainfall, evaporating it to dryness on a planchet 2.5 cm in diameter, and counting the activity. All radioactivity measurements were made with a Tracerlab low-background beta counting system with a background of about 0.8 count/min.

A day-to-day observation of each such sample showed no significant short-time decrease in activity until the occurrence of a heavy rainfall on 16 to 17 September 1968. This particular sample showed a rather abrupt increase in gross activity over that of the previous sample of 6 September (3950 count $\text{sec}^{-1} \text{ m}^{-2}$ as compared to 610 count $\text{sec}^{-1} \text{ m}^{-2}$) in addition to an apparent day-to-day decrease in activity.

Samples (each 3 liters) of the rainfall from 15 to 16 September and 3 October 1968 were analyzed for radioactive Ba^{140} and I^{131} by standard radiochemical procedures. A 12-liter sample of the rainfall from 5 October was analyzed for Ba^{140} . The results are shown in Table 1.

According to published news releases (2), U^{235} was used as the fissioning material for the French thermonuclear tests. In theory, it should therefore be possible to date the time

Table 1. Rainfall analyzed for radioactive Ba^{140} and I^{131} .

Rainfall date (1968)	Gross activity (count $\text{min}^{-1} \text{ m}^{-2}$)	Apparent half-life (gross activity in days)	Activity as of date of rainfall (disintegration $\text{min}^{-1} \text{ liter}^{-1}$)	
			Ba^{140}	I^{131}
13 August	103	> 100		
15 August	199	> 100		
25 August	422	> 100		
6 September	610	> 100		
15-16 September	3950	< 25	32.7 ± 3.5	4.7 ± 0.9
24 September	288	< 25	*	*
3 October	895	< 25	†	1.0 ± 0.2
5 October	980	< 25	5.8 ± 0.8	‡
9 October	215	~70		‡
13 October	78	~70	*	*
3 November	660	> 70		‡
10 November	218	> 100		
15 November	207	> 100		
23 November	240	> 100		
26-27 November	737	> 100		
30 November	176	> 100		
3 December	162	> 100		

* Analysis not attempted; less than 2 liters collected.

† Sample lost.

‡ Analysis run; no activity detected.