

THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF
N-FLUOROFORMYLIMINOSULFUR DIFLUORIDE AND
PENTAFLUOROSULFANYLIMINOSULFUR DIFLUORIDE,

by

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DOCTOR OF PHILOSOPHY

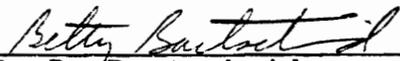
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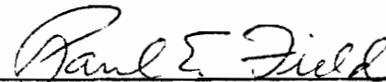
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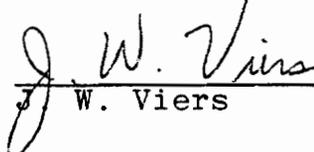
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to my parents

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INTRODUCTION

The investigation of the rotational spectra of fluoroformyliminosulfur difluoride, SF_2NCOF , and pentafluorosulfanyliminosulfur difluoride, SF_2NSF_5 , was undertaken to determine, from the experimental moments of inertia, the number and type of positional isomers and the bonding parameters. SF_2NCOF and SF_2NSF_5 are the first iminosulfur difluorides ($\text{RN}=\text{SF}_2$) to be investigated by microwave spectroscopy. The iminosulfur difluorides are characterized by a nitrogen-sulfur double bond with nonbonding pairs of electrons in an sp^2 hybridized orbital on the nitrogen atom and in an sp^3 hybridized orbital on the sulfur atom. This bonding scheme is expected to impart a unique charge distribution in the vicinity of the SF_2 fluorines. In SF_2NCOF the nitrogen-carbon bond may acquire some partial double bond character which can be described through resonance involving the S, N, C, and O atoms. The extent of this resonance would be expected to affect the length of the NC bond and to influence the height of the barrier to rotation about this bond.

For SF_2NCOF and SF_2NSF_5 , the question of cis-trans conformation about the nitrogen-sulfur double bond will be considered. Additionally, several rotameric forms of SF_2NCOF which can arise from rotation about the nitrogen-carbon axis and which cannot be definitely precluded by presumptive reasoning will also be examined.

A further aim of this study is to examine the utility of low resolution microwave spectroscopy when faced with the dilemma of a very rich spectrum and a multitude of plausible rotamers.

LOW RESOLUTION MICROWAVE SPECTROSCOPY

A. Introduction

Low resolution microwave spectroscopy (LRMW)^{1,2} came late to the subject of microwave spectroscopy following the introduction of broad-band rapid-scan microwave radiation sources. Since its inception, LRMW has become a powerful technique for conformational studies, while also serving to provide preliminary information for high resolution microwave experiments. In most cases LRMW does not provide information unobtainable by high resolution methods. It does, however, enable spectroscopists to rapidly study the rotational spectra of large, slightly asymmetric molecules for their conformational content.

As the complexity of a molecule increases, its rotational spectrum becomes more difficult, if not impossible, to interpret due to the sheer amount of information available. By lowering the resolution, the spectrum of a large, near symmetric top molecule is simplified to the extent that it resembles that of a symmetric top in appearance and in ease of analysis.

B. Theory

From the assignment of the appropriate rotational quantum numbers to the transitions of a high resolution microwave spectrum, the moments of inertia and, hence,

the molecular structure can, in principle, be determined. Analogously, by assigning the correct rotational quantum numbers to the 'bands' of a low resolution microwave spectrum, relatively accurate values of the moments of inertia are obtained. Then, from a knowledge of these moments the molecular conformation can, in favorable cases, be deduced.

When the microwave spectrum of a molecule can be described well by the rigid-rotor model, the rotational motion is determined by three principle moments of inertia.^{3,4} With the origin of the coordinate system at the center of mass, the principal moments of inertia are defined as

$$I_a \equiv \sum_i m_i r_{a_i}^2$$

$$I_b \equiv \sum_i m_i r_{b_i}^2$$

$$I_c \equiv \sum_i m_i r_{c_i}^2$$

where m_i is the mass of the i th atom and r_{a_i} , etc. is the perpendicular distance of the i th atom from the a -axis. In terms of these moments, the rotational constants are given as

$$A = \frac{h}{8\pi^2 I_a}$$

$$B = \frac{h}{8\pi^2 I_b}$$

$$C = \frac{h}{8\pi^2 I_c}$$

where h is Planck's constant. For an asymmetric rotor all three rotational constants are unequal.

The degree of asymmetry of an asymmetric rotor can be conveniently expressed as a simple function of the rotational constants by Ray's asymmetry parameter κ :

$$\kappa = \frac{2B - A - C}{A - C}$$

κ has the property of continuously varying between the oblate rotor limit: $\kappa = +1.0$ when $A = B$, and the prolate rotor limit: $\kappa = -1.0$ when $B = C$. The 'most asymmetric' rotor has a κ value of zero.

To facilitate the expression of the energy levels of a near prolate asymmetric top, Wang devised the following asymmetry parameter,

$$b_p = \frac{C - B}{2A - B - C}$$

where $b_p = 0$ and $b_p = -1$ correspond to the prolate symmetric top ($A \neq B = C$) and oblate symmetric top ($A = B \neq C$) limits, respectively.

In terms of the rotational constants and Wang's asymmetry parameter, the energy level expression of a near prolate asymmetric top has the form

$$E_{J_{K_{-1}K_{+1}}} = \frac{1}{2}(B+C)J(J+1) + \left[A - \frac{1}{2}(B+C) \right] E_{J_{K_{-1}K_{+1}}}(b_p)$$

where the reduced energy $E_{J_{K_{-1}K_{+1}}}(b_p)$ can be approximated by a power series expansion in b_p :

$$E_{J_{K_{-1}K_{+1}}}(b_p) = K_{-1}^2 + c_1 b_p + c_2 b_p^2 + c_3 b_p^3 + \dots$$

The notation $J_{K_{-1}K_{+1}}$ specifies a particular rotational energy level: J is the total angular momentum quantum number and K_{-1} and K_{+1} are pseudoquantum numbers representing the prolate and oblate symmetric rotor limits, respectively. The number of perturbation coefficients c_i to be used in the expansion is dictated by the size of the asymmetry parameter b_p . A greater degree of molecular asymmetry necessitates the inclusion of additional c_i 's in the reduced energy expression. Conversely, the reduced energy expression can be truncated when the asymmetry of the molecule approaches that of a symmetric top.

For the analysis of a low resolution spectrum of an asymmetric rotor near the prolate limit, i.e. $b_p \sim 0$, the energy level expression may be further simplified to give

$$E_{J_{K_{-1}}} = \left(\frac{B+C}{2}\right)J(J+1) + \left(A - \frac{B+C}{2}\right)K_{-1}^2$$

where the reduced energy expression has been approximated by K_{-1}^2 .

The frequency of 'permissible' absorptions is determined from the above expression by employing the Bohr condition

$$\nu = \frac{\Delta E_{\Delta J \Delta K_{-1}}}{h}$$

and the selection rules:

$$\Delta J = 0, \pm 1$$

$$\Delta K_{-1} = 0, \pm 1 .$$

Dipole absorptions which involve a nonzero dipole component along the a-axis are termed parallel or a-type transitions. Additionally, because the a-type transitions are governed by the selection rules: $\Delta J = 1, \Delta K = 0$, they are called ^aR-type transitions. Since there are $(2J+1)$ distinct sublevels for every J level of an asymmetric top, each change in J results in $(2J+1)$ transitions. For a slightly asymmetric rotor these $(2J+1)$ transitions will be nearly co-incident in frequency. Under low-resolution conditions, these nearly degenerate transitions and their attendant vibrational satellites are observed

as broad bands. Thus, the $3 \leftarrow 2$ aR band will be the superposition of the following absorptions:

$$3_{13} \leftarrow 2_{12}$$

$$3_{01} \leftarrow 2_{02}$$

$$3_{22} \leftarrow 2_{21}$$

$$3_{21} \leftarrow 2_{20}$$

$$3_{12} \leftarrow 2_{11}$$

where the notation $J'_{K_{-1}K_{+1}} \leftarrow J_{K_{-1}K_{+1}}$ is used.

The peak frequency of the aR -type bands can be fitted approximately to an equation of the form

$$\nu = (B+C)(J+1) \quad .$$

The equally spaced aR -type bands, whose interval of separation is $B+C$, are the analogous transitions of a symmetric top, having a reciprocal moment of $B+C$. Thus, they are responsible for the pseudo-symmetric top appearance of LRMW spectra. The aR -type bands can be fitted to the above equation by dividing the frequency of the band centers by successive values of $J+1$, an integer quantity, until a constant value of $B+C$ is approached. Then, an average $B+C$, which closely approximates B_0+C_0 (the effective ground-state rigid rotor rotational constant) can be found.

A second kind of aR -type band, termed Type II, is occasionally observed for near-prolate asymmetric top molecules.⁵ Normally, only molecules with an asymmetry parameter in the approximate range $-0.5 \geq \kappa \geq -0.7$ exhibit Type II bands. Type II bands are comprised of transitions of the type $(J+1)_0 J+1 \leftarrow J_0 J$ and $(J+1)_1 J+1 \leftarrow J_1 J$ along with their attendant vibrational satellites.

In contrast to the previously mentioned aR -type bands, the energy level expression for aR -type II bands follows from the oblate energy level expression:⁶

$$E_{J_{K_{-1}K_{+1}}} = \frac{1}{2}(A+B)J(J+1) + \{C - \frac{1}{2}(A+B)\}\{K_{+1}^2 + c_1 b_0 + c_2 b_0^2 + \dots\}$$

where b_0 , the oblate asymmetry parameter, has the form

$$b_0 = \frac{A-B}{2C-B-A} .$$

For a molecule not too far on the prolate side, i.e. $\kappa \leq -0.7$, terms in b_0 can be neglected; the truncated energy level expression becomes

$$E_{J_{K_{+1}}} = \frac{1}{2}(A+B)J(J+1) + \{C - \frac{1}{2}(A+B)\}\{K_{+1}^2\} .$$

The frequency of the aR -type II band maxima, which is found from the above expression by employing the selection rule $J+1 \leftarrow J$ and by the substitution $K_{+1} = J$, is written as

$$\nu = 2C(J + \frac{1}{2}) + \frac{1}{2}(A+B) .$$

The regularly spaced aR -type II bands are separated by $\nu 2C$ and the frequency of the band center divided by the spacing is $\nu J + \frac{1}{2} + (A+B)/4C$. Thus, an estimate of the C rotational constant can be made from the separation of adjacent bands. This value of C when used in conjunction with a minimum of two experimental band centers allows one to find $A+B$.

If, in addition to the μ_a dipole component, there is a nonzero component of the dipole normal or perpendicular to the a -axis (symmetry axis), absorptions involving this component may also be seen. This perpendicular component will lie along either the b or c principle axis. Thus, one might observe either bR - or cR -type transitions, depending upon the component of the dipole present. For a near-prolate asymmetric rotor, the frequency of these transitions, as calculated from the prolate energy level expression with the selection rules $\Delta J = 1$, $\Delta K_{-1} = 1$, is

$$\nu = (B+C)(J+1) + (2A-B-C)(K_{-1} + \frac{1}{2}) \quad .$$

Additionally, the selection rules $\Delta J = 1$, $\Delta K_{-1} = 1$ may lead to bP - or cP -type transitions whose frequency is given by

$$\nu = -(B+C)J + (2A-B-C)(K_{-1} + \frac{1}{2}) \quad .$$

Generally, bR -, cR -, bP -, and cP -type transitions are not only weak, but are also widely scattered throughout the

spectrum. Consequently, they cannot be artificially condensed to give bands in a LRMW spectrum and will not be further considered.

The perpendicular dipole component may also give rise to bQ - or cQ -type transitions which obey the selection rules $\Delta J = 0$, $\Delta K_{-1} = 1$. Under low-resolution condition the Q-branch transitions, which are nearly co-incident in the spectrum of a near-prolate asymmetric rotor, become superimposed, leading to bands occurring at

$$\nu = (2A-B-C)(K_{-1} + \frac{1}{2}) .$$

These bands, therefore, form a series with a spacing of $2A-B-C$ and with the property that the frequency of the band centers divided by the spacing is equal to $K_{-1} + \frac{1}{2}$, which will be a half-integer quantity.

Usually the Q-type bands are weaker and broader than the R-type bands.⁷ This is due, in part, to the greater spreading of the Q-branch transitions over a wider frequency range and to a frequently occurring small perpendicular dipole component. This spreading effect is most severe for the Q-branch transitions with the highest J and the highest intensity. As a result, converging transitions that lead to Q bands are of low J and of low intensity. Because of their greater tendency to diverge, Q bands sometimes appear as jagged doublets rather than as the smoothly contoured envelopes which characterize

the R bands.

A summary of the allowed absorptions for a near-prolate asymmetric rotor is given in Table I.

C. Experimental

The lowering of the available resolution to produce a LRMW spectrum is accomplished by a fast sweep rate (~ 10 MHz/sec) in conjunction with a long detector time constant ($\sim 0.3 - 3.0$ sec) and a high sample pressure (> 20 mtorr).² These recording conditions, however, distort the band-shape and position. Therefore, it is necessary to average the frequency of the band maxima over forward and reverse scans.

Because recording a band spectrum necessitates sweeping over several thousand megahertz at the rate of ~ 10 MHz/sec, a broad-band rapid-scan microwave spectrometer is required. Since most modern microwave laboratories already have high resolution spectrometers of this design, no additional microwave hardware or equipment modification is necessary.

A Stark sample cell is preferred over a frequency modulated sample cell due to the enhanced sensitivity. The Stark cell should be operated at the highest practical Stark voltages to minimize interference from Stark components. A means of cooling the cell is desirable if thermo-

Table I
 Summary of Permissible Transitions of a Near Prolate Asymmetric Rotor

Selection Rules	Transition Type	Frequency	Give Rise to LRMW Bands?
$\Delta J = 1 \quad \Delta K_{-1} = 0$	R	$\nu = (B+C)(J+1)$	Yes
$\Delta J = 1 \quad \Delta K_{+1} = 0$	R	$\nu = 2C(J + \frac{1}{2}) + \frac{1}{2}(A+B)$	Yes
$\Delta J = 1 \quad \Delta K_{-1} = 0$	R	$\nu = (2A-B-C)(K_{-1} + \frac{1}{2}) + (B+C)(J+1)$	No
$\Delta J = 1 \quad \Delta K_{-1} = 0$	P	$\nu = (2A-B-C)(K_{-1} + \frac{1}{2}) - (B+C)J$	No
$\Delta J = 0 \quad \Delta K_{-1} = 1$	Q	$\nu = (B+C)(J+1)$	Yes

dynamic data is to be extracted from the low resolution data.

D. Sample Requirements

In order for a molecule to exhibit a well-defined band spectrum it must be a near-symmetric top, i.e., $|K| \geq 0.7$. This restriction may be overcome in certain instances by the substitution of a bulky group with quasi-axial symmetry, e.g., t-butyl or phenyl, or a heavy atom, e.g., iodine or bromine, on the symmetry axis. This procedure will impart the necessary symmetry when one is interested in the conformation of a certain moiety in the molecule.

Under high-resolution conditions, rotational transitions from a dipole component of a few hundredths of a debye are observable. For low resolution work, however, a dipole component of at least 0.5 - 1.0D is necessary in order to provide a reasonable S/N.

The sample must be volatile; a vapor pressure of ~ 20 mtorr at the operating temperature of the spectrometer is usually required. In cases where low volatility poses a problem the preparation of derivatives is often helpful.

The question of purity can be crucial when the impurity gives a similar spectrum to the molecule of interest. In the rare event that the bands for an impurity do overlap with those of the compound under study, chromatographic

methods can be used to easily achieve an impurity level of 0.1% - the low resolution detection limit of an impurity having comparable line strengths. Small molecules, though they are polar and volatile, are not troublesome impurities. Their rotational spectra, even under low resolution conditions, consist of narrow lines which are easily discernible.

Lastly, there is a limit on the molecular size which can be studied profitably by LRMW. If the molecule is very large, B+C will be small, resulting in band-overlap and poor resolution. For good resolution, B+C must be greater than 500 MHz.

E. Band Intensity

The intensity of the aR -type bands increases with increasing value of the rotational constant, J. At higher J values, there are more high K_{-1} components which are shifted relatively little from the symmetric rotor frequency. This results in a greater availability of lines of nearly coincident frequency, which can then be successfully integrated under a single envelope, producing a more intense band. The above-mentioned correlation of band intensity with J will eventually be offset by a decrease in the shift of the Stark components as very high J (~ 40) is approached. Ultimately, it will become impossible to modulate high J

lines even at the highest physically achievable Stark fields; no LRMW spectrum will be observed.

Another factor which affects the band intensity is the frequency of the band maxima. Since the intensity of the band maxima depends upon the square of the frequency, there is a pronounced increase of intensity with frequency.

F. Band Width

The band width of a LRMW spectrum is largely controlled by the molecular asymmetry. A greater degree of asymmetry leads to a larger separation between individual transitions. This effect will not only produce broader bands, but will also lead to a weaker and a more diffuse band spectrum.

Steinmetz⁸ has observed that a reasonable correlation exists between the asymmetry κ and the band width at half-intensity. This correlation allows one to make a semi-quantitative measure of the expected molecular asymmetry by comparing observed band widths to those of molecules with known asymmetry. The dependence of band width of ^aR-type bands at half-height on κ for several molecules of widely varying rotational constants is given in Table II. Due to the paucity of observed Q-bands no such correlation can presently be made for them.

Table II
Dependence of Band Width on Asymmetry

Molecule	Band Width MHz	κ
<u>trans</u> -Cinnamaldehyde	64	-0.97
Iodobenzene	65	-0.96
p-Anisonitrile	68	-0.95
p-Nitroanisole	68	-0.95
p-Anisaldehyde		
s-Trans conformer	62	-0.95
s-Cis conformer	92	-0.93
α -Ionone	100	-0.85
β -Ionone	180	-0.81

G. Conformational Analysis

The subject of internal motion and molecular conformation of small molecules is of special interest to scientists involved with enzyme, protein, and polymer studies.⁹ It is believed that an understanding of these phenomena in relatively small molecules may render some insight into those of larger and less easily studied molecules, e.g., polymers and biological molecules.

High resolution microwave spectroscopy has been the preferred structural technique for the study of internal motions and molecular conformations of small molecules for a number of years.¹⁰ The interconversion between rotameric species is primarily controlled by thermal collisions. On the time-scale of the microwave experiment, the time between thermal collisions is very long. Thus, each conformer in a mixture of conformers can be viewed as a separate entity, even though the interconversion is of such rapidity that chemical separation becomes impossible. Additionally, since different configurations of a molecule generally have quite different moments of inertia, each conformer gives a distinguishable microwave spectral pattern. In suitable cases, then, it becomes possible to extract the molecular structure, dipole moment, barriers to internal rotation, nonbonded distances, and torsional frequencies for each conformer present. Although nuclear magnetic resonance,

infrared absorption, and electron diffraction, as well as chemical means, can be used to study certain aspects of molecular motion, these techniques cannot give all the information provided by the analysis of a pure rotational spectrum.

Of late, microwave spectroscopists have learned that valuable conformational information can be gleaned rather quickly on large, flexible, molecules from the analysis of the low resolution microwave spectrum.^{11,12} This analysis can provide information concerning:

Conformational preference about single bonds

Ring conformation

Side chain position

Barrier heights and thermodynamic data, e.g.,
 ΔE , ΔH , and ΔG

Number of stable conformers

Relative abundance of conformers

In the absence of any observable isotopic species, the number of different band series in a low resolution spectrum directly gives the number of near prolate or oblate conformers present. Furthermore, provided the conformational changes of the system studied are sensitive to changes in $B+C$ and/or $2A-B-C$, one can obtain the stereochemistry for each conformer observed by comparing the calculated and observed rotational constants. To make this comparison, one must first assume an initial structure. A reasonable

approximation of the structure can be made by compounding known bonding parameters from similar molecules. Once a set of bonding parameters has been assumed, the conformation of the molecule is varied, i.e., the dihedral angles are changed and the rotational constants for the various positional isomers are calculated. Insofar as only changes in dihedral angles, and not changes in bonding parameters, are concomitant with conformational changes, then rotational constants can be calculated from assumed structures with a confidence of 5% or better.

Upon examination of the calculated rotational constants, one or more conformers may be ruled out if the rotamer is predicted to be too asymmetric to give a measurable LRMW spectrum. Other conformers may be eliminated based on polarity, or chemical and other spectral evidence. For the plausible isomeric forms which pass the elimination processes, one may then, within reason, adjust the molecular dimensions until the calculated rotational constants are brought into agreement with those from experiment. At this point, one must realize that any attempt to force exact agreement between theory and experiment in hopes of obtaining better molecular dimensions is more lucrative for a high resolution study than for a low resolution study.

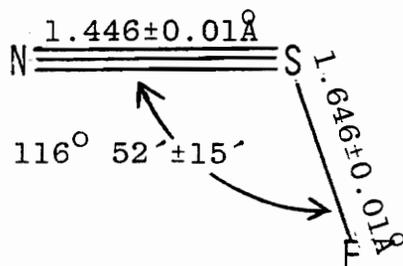
REVIEW OF PRIOR RESEARCH

Nitrogen-sulfur-fluorine chemistry^{13,14} provides a rich collection of small, volatile, polar molecules with varied properties, reactivities, and stabilities amenable for structural analysis by rotational spectroscopy and by electron diffraction. These two gas-phase structural techniques have proven valuable for not only structural information, but also for authentication of the existence of a certain N-S-F containing species.

The first nitrogen-sulfur-fluorine containing molecule for which the structure was determined was thiazyl trifluoride. From the assignment of the rotational spectrum of thiazyl trifluoride, Kirchhoff and Wilson¹⁵ found the structure to be $\text{N}\equiv\text{S}\begin{matrix} \text{F} \\ \diagup \\ \text{F} \\ \diagdown \end{matrix}$, rather than the isomers $\begin{matrix} \text{F} \\ \diagdown \\ \text{S}=\text{N}-\text{F} \\ \diagup \\ \text{F} \end{matrix}$ or $\text{S}-\text{N}\begin{matrix} \text{F} \\ \diagup \\ \text{F} \\ \diagdown \end{matrix}$ as proposed by some previous investigators. Since NSF_3 is a symmetric top, only three bonding parameters are needed to completely determine its structure. An r_0 structure having: $r_{\text{N}=\text{S}} = 1.416 \pm 0.003\text{A}$, $r_{\text{S}-\text{F}} = 1.552 \pm 0.003\text{A}$ and $\angle\text{NSF} = 94^\circ 2' \pm 16'$ was determined from the assignment of the four isotopic species: $^{14}\text{N}^{32}\text{SF}_3$, $^{14}\text{N}^{33}\text{SF}_2$, $^{14}\text{N}^{34}\text{SF}_2$ and $^{15}\text{N}^{32}\text{SF}_3$.

Kirchhoff and Wilson¹⁶ also determined the structure of thiazyl fluoride from its rotational spectrum. Prior to their microwave study, infrared absorption, nuclear magnetic resonance, electron diffraction studies, and

hydrolysis experiments favored either the isomer $S\equiv N-F$ or $N\equiv S-F$. From the assignment of the rotational spectra of two isotopic species, $N^{32}SF$ and $N^{34}SF$, the structure was established unambiguously to be:



Of special importance to the present investigation are the structures of chloroiminosulfur difluoride, SF_2NCl , and trifluoromethyliminosulfur difluoride, SF_2NCF_3 . They contain the iminosulfur difluoride moiety, $-N=SF_2$, in common with SF_2NCOF and SF_2NSF_5 . The geometrical and rotational isomerization and the bonding parameters of SF_2NCl and SF_2NCF_3 have been investigated by infrared absorption and electron diffraction methods.

Only one geometrical and one rotational isomer of SF_2NCl was detected in the gas-phase electron diffraction¹⁷ and infrared studies¹⁸ by Glemser. A cis conformation about the $N=S$ bond was found, with the S, N, and Cl atoms lying in a symmetry plane which bisects the FSF angle. Figure I gives the reported bonding parameters consistent with the electron diffraction data.

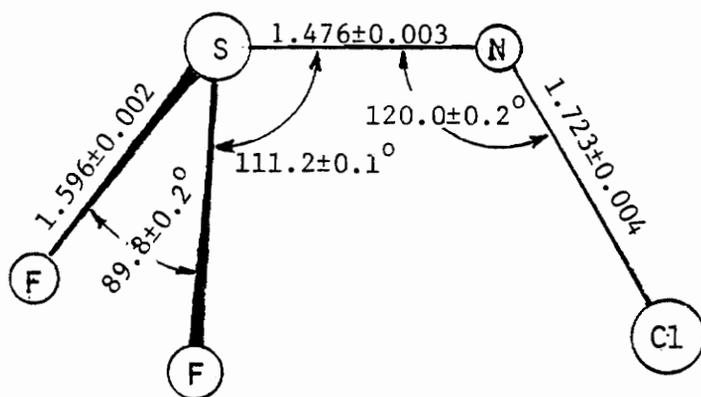
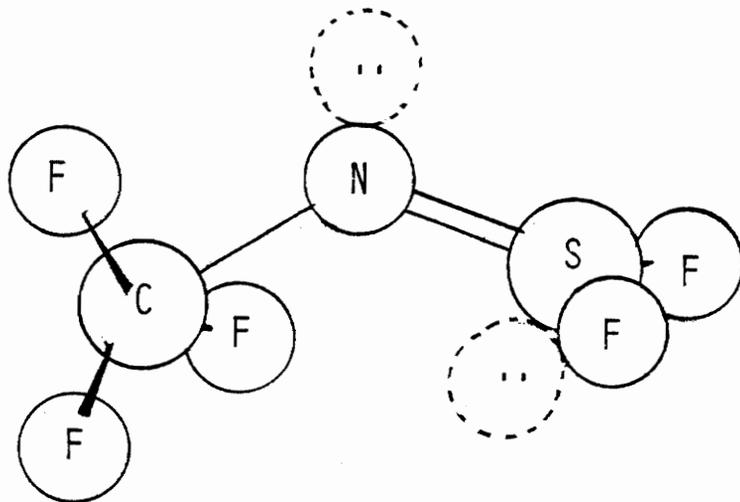


Figure I. Gas-Phase Electron Diffraction Structure of Chloroiminosulfur Difluoride

The geometrical and rotational isomerization of trifluoromethyliminosulfur difluoride was initially studied by infrared spectroscopy.¹⁹ SF_2NCF_3 has two conformational degrees of freedom: rotation of the CF_3 unit relative to the NSF_2 entity. Rotation of the former kind, whereby two asymmetric units rotate about the $\text{N}=\text{S}$ double bond, could lead to the possible existence of two or more positional isomers. However, rotation of the latter type, which involves rotation of a symmetric unit, CF_3 , about a $\text{C}-\text{N}$ single bond, may or may not give rise to detectable isomerization.

Since little or no evidence for the presence of two or more rotational isomers was seen in the infrared spectrum of SF_2NCF_3 , Griffiths¹⁹ concluded that the conformation about the $\text{N}=\text{S}$ bond is frozen in either the cis or trans conformation (see Figure II), and that either the CF_3 unit is frozen in position or freely rotating. Albeit naive, Griffiths selects, based on natural selection of a symmetric structure over an asymmetric one and on steric effects, the trans conformer as best representing the minimum energy configuration for SF_2NCF_3 . There is support, based on an electron diffraction study by Karl and Bauer²⁰, for a frozen conformation about the $\text{N}=\text{S}$ bond. They found the minimum energy conformation to be essentially cis about the double bond. This conclusion resulted from a test of

Trans-



Cis-

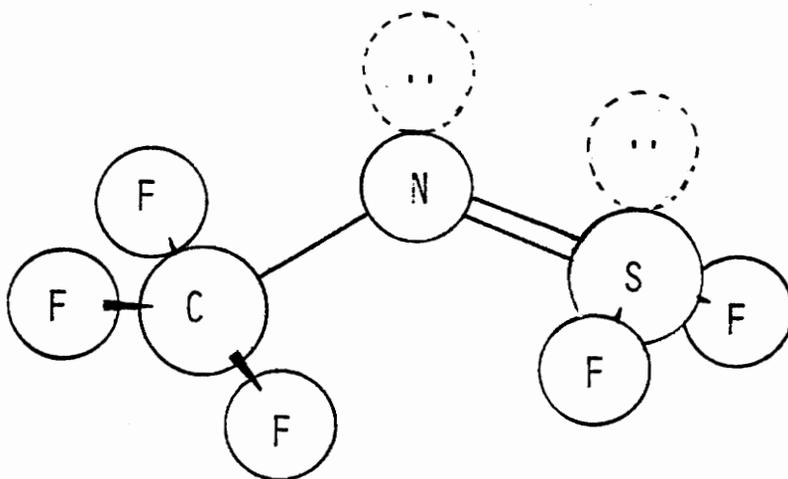


Figure II. Cis and Trans Conformations of Trifluoromethyliminosulfur Difluoride

a wide range of models covering many positional isomers about the N=S and N-C bonds. Evidence for a second isomer with either a trans or a gauche configuration about N=S was not observed. The reported structure is illustrated in Figure III.

Considering pentafluorosulfanyliminosulfur difluoride, SF_2NSF_5 , to be a monosubstituted derivative of sulfur hexafluoride, the structures of SF_6 ,²¹ SF_5Cl ,²² SF_5OF ,²³ and SF_5NF_5 ²⁴ are germane to the present investigation. Figure IV contains the structures consistent with the diffraction and spectroscopic data for these molecules. Of particular interest is the question: How greatly do the derivatives depart from the octahedral symmetry of SF_6 ? On the basis of steric effects and electronegativity, one would expect some distortion of the O_h symmetry in these derivatives. This distortion would also be expected to manifest itself in the values of the $F_{eq}SF_{ax}$ angle and the $F-S_{ax}$ bond length. As can be seen in Figure IV, the distortion of the O_h symmetry in the derivatives, while quite observable, is slight.

Although no detailed structural studies have been reported on SF_2NCOF and SF_2NSF_5 , Shanzer²⁵ has reported both a theoretical and a temperature-dependent ^{19}F -NMR conformational study on these molecules, as well as on various other SF_2NR molecules ($R = F, CN, CF_3, COCH_3$, and

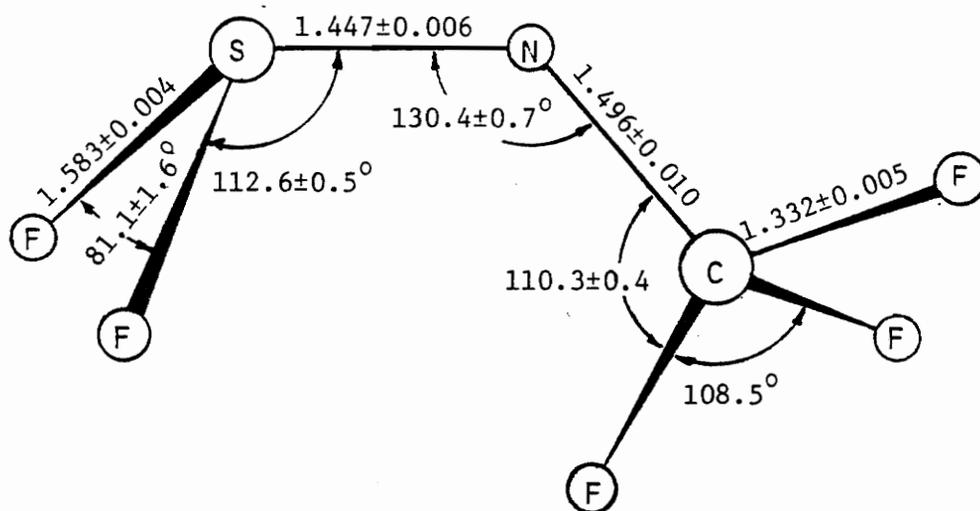
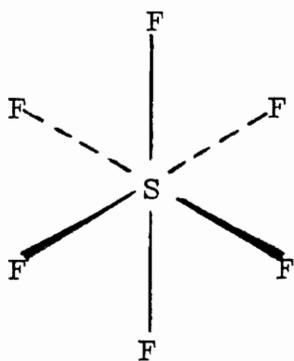
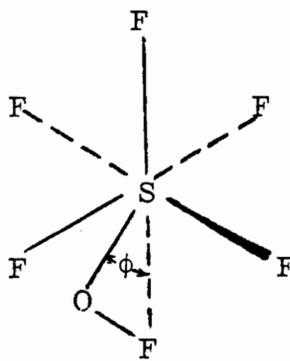


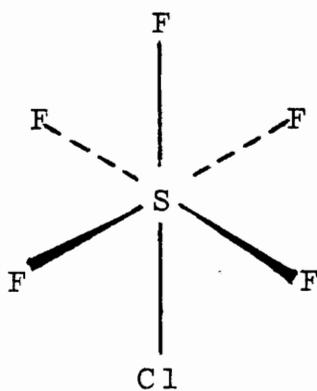
Figure III. Gas-Phase Electron Diffraction Structure of Trifluoromethyliminosulfur Difluoride



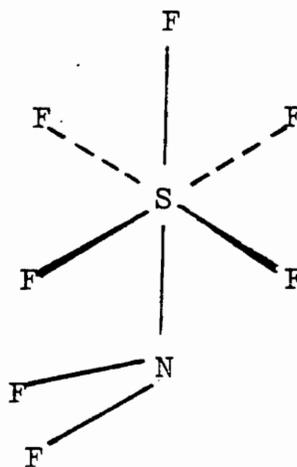
$$\begin{aligned} \text{S-F} &= 1.56 \pm 0.02 \text{ \AA} \\ \langle \text{FSF} &= 90^\circ, 180^\circ \end{aligned}$$



$$\begin{aligned} \text{S-F} &= 1.530 \pm 0.005 \text{ \AA} \\ \langle \text{FSF} &= 90^\circ, 180^\circ \\ \phi &= 2^\circ \end{aligned}$$



$$\begin{aligned} \text{S-F} &= 1.576 \pm 0.010 \text{ \AA} \\ \langle \text{F}_a \text{SF}_e &= 88^\circ 22' \pm 10' \\ \langle \text{F}_e \text{SF}_e &= 90^\circ \text{ (Assumed)} \end{aligned}$$



$$\begin{aligned} \text{S-F}_a &= 1.560 \pm 0.007 \text{ \AA} \\ \text{S-F}_e &= 1.546 \pm 0.002 \text{ \AA} \\ \text{S-N} &= 1.696 \pm 0.005 \text{ \AA} \\ \langle \text{F}_a \text{SN} &= 179.5 \pm 0.6^\circ \\ \langle \text{F}_a \text{SF}_e &= 90.0 \pm 0.3^\circ \end{aligned}$$

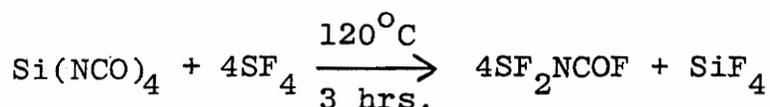
Figure IV. Some Gas-Phase Structures of Molecules Containing the Pentafluorosulfanyl Moiety, $-\text{SF}_5$

Ø). From CNDO molecular orbital calculations of the total energies of SF_2NCOF and SF_2NSF_5 as a function of rotation about the N=S bond, Shanzer found two minima of equal energy, separated by a low-lying maximum. The total energy curve was interpreted as an example of essentially free rotation about the N=S bond, whereby thermal excitation of a few kcal could give rise to various rotamers of SF_2NCOF and SF_2NSF_5 . Additionally, the appearance of resolvable spin-spin splitting at -80°C in the NMR spectrum, while the room temperature spectrum was devoid of such fine structure, is cited as evidence of conformational changes in SF_2NCOF .²⁵ Likewise, temperature-dependent spectral changes in the ^{19}F -NMR spectrum of SF_2NSF_5 are explained as cessation of free rotation about the N=S bond as lower temperatures are approached.²⁵

THE MICROWAVE SPECTRUM OF
N-FLUOROFORMYLIMINOSULFUR DIFLUORIDE

A. Experimental

The N-fluoroformyliminosulfur difluoride used for this study was synthesized by D.E. Maurer and J.S. Thrasher of the Department of Chemistry at Virginia Polytechnic Institute and State University. The synthetic route²⁶ used in the preparation



gives a yield of 80% with the major impurities being SiF_4 , COF_2 , and an isocyanate.

Trace impurities of COF_2 and HNCO were detected in the initial microwave spectrum. However, SiF_4 was not detected in the spectrum since it has no permanent electric dipole moment. The impurities were removed by vacuum distillation using traps at -196°C and -78°C , while holding the sample at -45°C . The purity of the distillate was ascertained from its infrared and mass spectra and from the absence of impurity lines in the microwave spectrum.

N-Fluoroformyliminosulfur difluoride undergoes thermal degradation to COF_2 and NSF .²⁷ During the course of this investigation, it was necessary to perform repeated distillations and to store the sample at dry ice temperature in order to maintain sample integrity.

The microwave spectrometer used in this investigation was a typical 36Kc/sec Stark modulated, laboratory-constructed spectrometer. Figure V contains a schematic of the spectrometer. A 8690B Hewlett-Packard Sweeper with a Backward Wave Oscillator (BWO), phased-locked to a HP8466A reference oscillator, served as the microwave radiation source. The vapor of the sample under study was contained in the Stark cell, a ten foot length of X-band copper waveguide with hermetically sealed mica windows. A septum of nickel plated phosphor-bronze, supported by flat strips of Teflon, were constructed to lie flush with the inside (narrow) walls and to run the length of the guide. Between the septum and the guide, a 0-1000 volt zero-based square wave potential could be controllably applied, thus allowing modulation of resonance frequencies via the Stark effect. Stark voltages were applied to the cell using a laboratory-built square wave generator of the De Wijn²⁸ design.

The band spectra of N-fluoroformyliminosulfur difluoride were recorded at two temperatures: room temperature and a low temperature (-68°C to -72°C) with the Stark cell surrounded in crushed dry ice. At these two temperatures the spectra were virtually identical both qualitatively and quantitatively. A portion of the cooled spectrum follows in Figure VI. Samples of SF_2NCOF in normal isotopic abundance were degassed and distilled into the

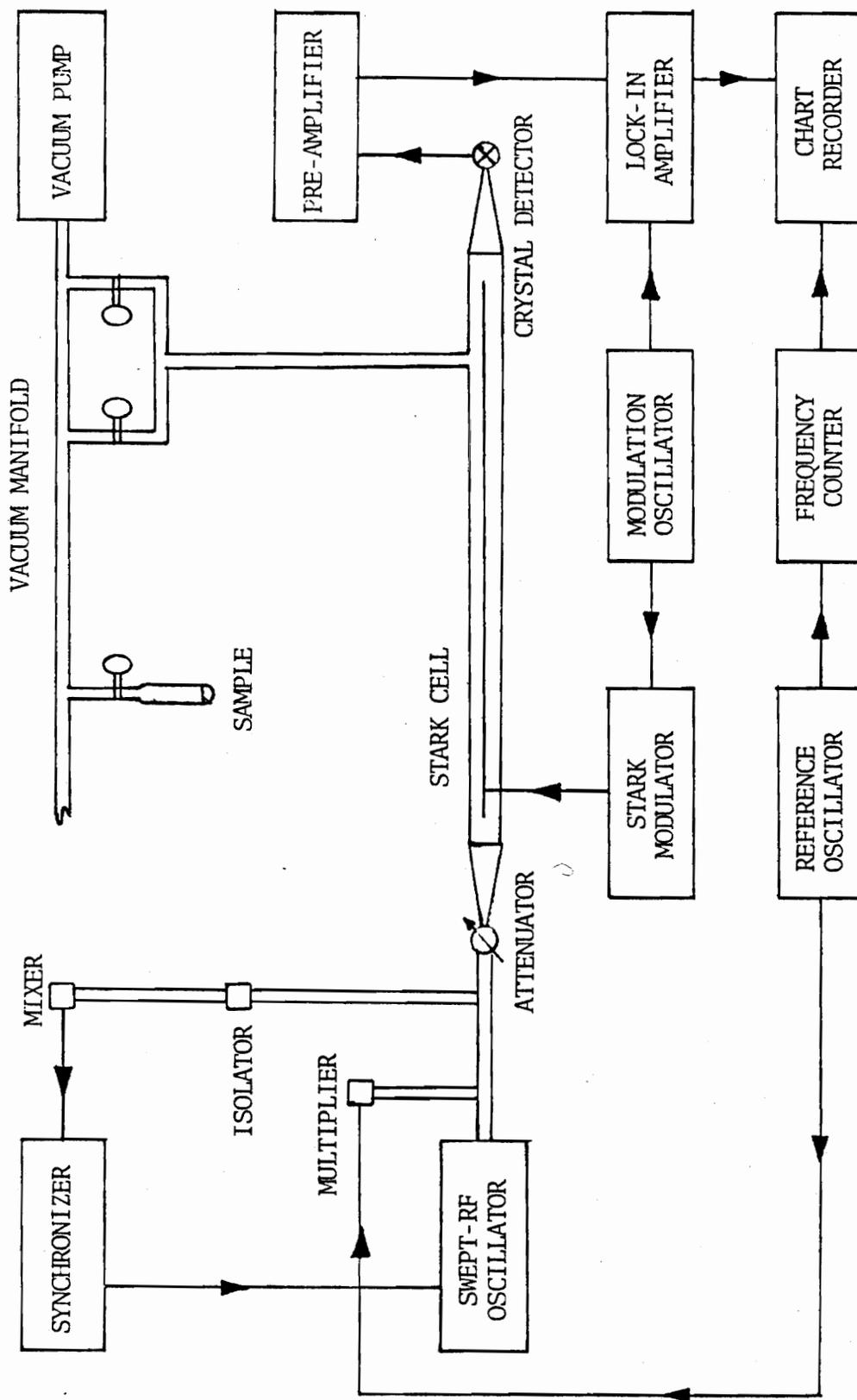


Figure V. Stark-Modulated Microwave Spectrometer

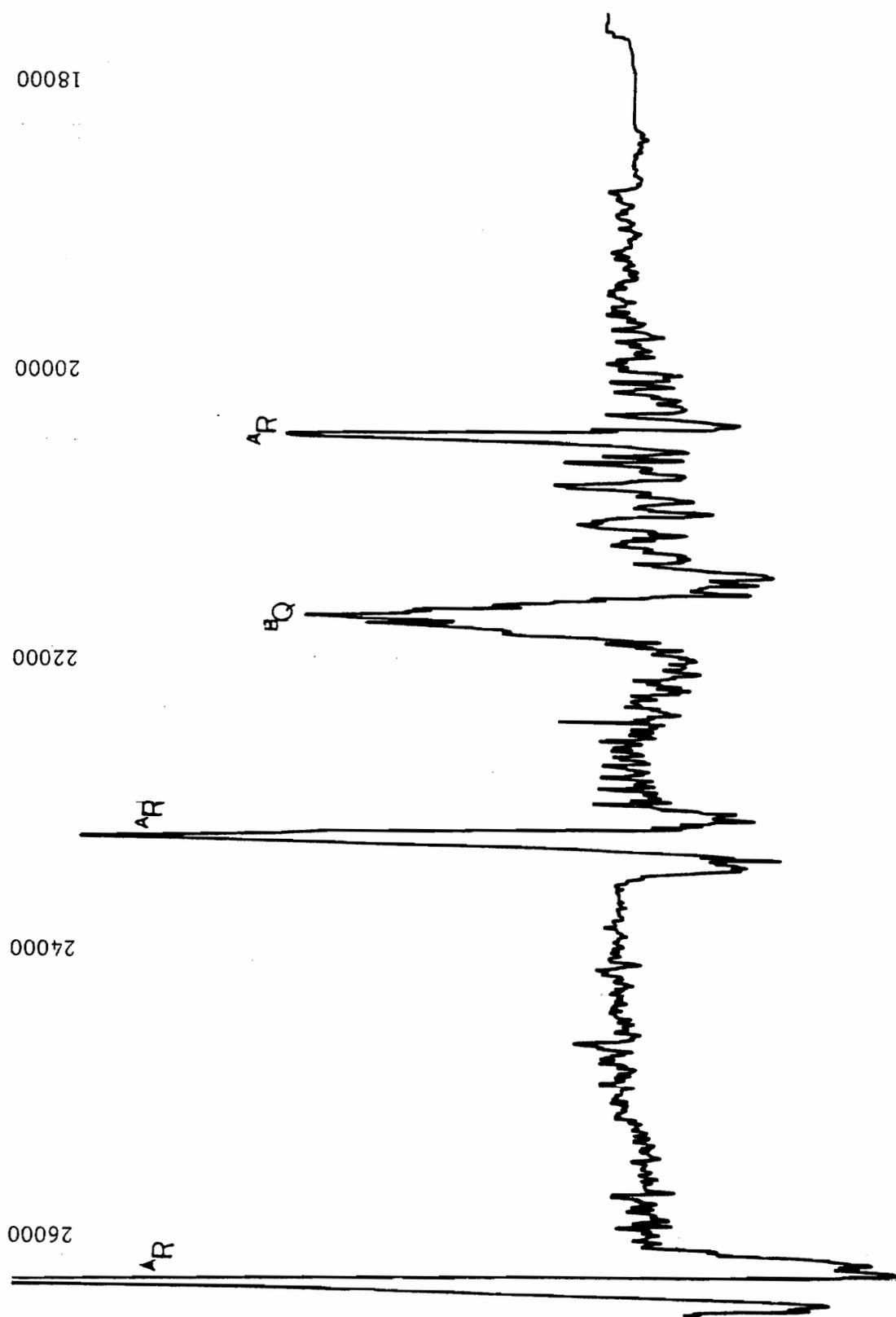


Figure VI. Low Resolution Microwave Spectrum of n-Fluoroformyliminosulfur Difluoride

absorption cell to pressures of about 20μ with a Stark potential of 1000 volts base-to-peak. A scan rate of 10 MHz/sec coupled with a lock-in detector time constant of 1.0 sec was usually employed.

Interpolation from 100 MHz markers recorded on the spectra was used to determine the frequencies of the band peaks. Frequency accuracy was dependent upon the band shape and band width and varied from 10 MHz for the aR -type bands to 50 MHz for the broader bQ -type bands. The band centers were measured using both up and down scans and the averages were used to determine the rotational parameters.

Five aR -type bands and two bQ -type bands were observed in the 12.5 - 26.5 GHz region and were assigned to the normal isotopic species. Table III summarizes the band assignments. The uncertainties listed for B+C and 2A-B-C represent estimated uncertainties of the frequencies of the aR -type and the bQ -type band maxima divided by the average $(J+1)$ value and the average $(K_{-1} + \frac{1}{2})$ values, respectively.² Bands due to less abundant isotopes were not observed; Table IV lists the sulfur isotopes and their relative natural abundance.

All high resolution spectra of N-fluoroformylimino-sulfur difluoride were recorded at dry ice temperature with a sample pressure of 5-10 μ . Because relative line intensity aided in the spectral assignment, care was exercised

Table III.
 Low Resolution Microwave Spectral Data of
 N-Fluoroformyliminosulfur Difluoride

^aR-type Bands

J+1	ν (MHz)	B+C(MHz)
5	14570 \pm 10	2914 \pm 2
6	17480	2913
7	20390	2913
8	23300	2913
9	26210	2912

^bQ-type Bands

$K_{-1} + \frac{1}{2}$	ν (MHz)	2A-B-C(MHz)
2.5	15620 \pm 50	6248 \pm 20
3.5	21740	6211

Table IV
Relative Abundances of Naturally Occuring Sulfur Isotopes^a

Mass Number	Atomic Weight (amu)	% Abundance	Nuclear Spin
32	31.9720737	95.0	0
33	32.971462	0.760	3/2
34	33.967865	4.22	0
36	35.967090	0.0136	0

a. Values taken from W. Gordy and R. L. Cook, Microwave Molecular Spectra (Interscience, New York, 1970).

to maintain the sample temperature, the sample pressure, the crystal current, and the settings of the recorder and detector constant while each spectrum was recorded. Moreover, to ensure that each line measured was fully modulated, each spectrum was recorded at various Stark voltages. The frequencies of the rotational transitions were measured by using frequency markers at 1.0 MHz intervals.

The spectrum contained numerous absorptions with unclear Stark effects - typical of a large, flexible molecule. Line-widths of 1.5 - 2.0 MHz at half-intensity were frequently observed and were attributed to unresolved nitrogen-14 quadrupole hyperfine-splitting and unresolved vibrational satellites.

In the ground vibrational state, 65 rotational transitions of the $^{32}\text{SF}_2\text{NCOF}$ species and 12 rotational transitions of the $^{34}\text{SF}_2\text{NCOF}$ species were assigned. Tables V and VI list the respective assignments of $^{32}\text{SF}_2\text{NCOF}$ and $^{34}\text{SF}_2\text{NCOF}$.

B. Low Resolution Microwave Spectrum and Conformation of N-Fluoroformyliminosulfur Difluoride

N-Fluoroformyliminosulfur difluoride has two conformational degrees of freedom: rotation of the COFN unit relative to the SF_2 moiety and rotation of the COF unit relative to the NSF_2 entity. Both types of rotational isomerization can lead to two or more different stable configurations. Notwithstanding the possibility of several isomers of

Table V
Spectral Assignment of $^{32}\text{SF}_2\text{NCOF}^a$
(MHz)

Transition	Frequency
$4_{23} - 3_{12}$	20852.5
$4_{22} - 3_{13}$	21100.9
$5_{24} - 4_{13}$	23685.6
$5_{23} - 4_{14}$	24101.2
$6_{16} - 5_{05}$	20170.3
$6_{25} - 5_{14}$	26496.5
$7_{07} - 6_{06}$	20369.5
$7_{17} - 6_{16}$	20245.4
$7_{16} - 6_{15}$	20530.4
$7_{26} - 6_{25}$	20388.9
$7_{25} - 6_{24}$	20412.3
$7_{17} - 6_{06}$	22954.0
$8_{08} - 7_{07}$	23273.2
$8_{18} - 7_{17}$	23138.2
$8_{17} - 7_{16}$	23460.3
$8_{27} - 7_{26}$	23302.1
$8_{26} - 7_{25}$	23336.8
$8_{08} - 7_{17}$	20694.6
$8_{18} - 7_{07}$	25718.3

Continued

Continuation of Table V
Spectral Assignment of $^{32}\text{SF}_2\text{NCOF}^a$
(MHz)

Transition	Frequency
$^9_{09} - ^8_{08}$	26172.9
$^9_{19} - ^8_{18}$	26027.8
$^9_{18} - ^8_{17}$	26390.0
$^9_{28} - ^8_{27}$	26210.4
$^9_{09} - ^8_{18}$	23731.3
$^{11}_{111} - ^{10}_{28}$	21166.3
$^{11}_{110} - ^{10}_{29}$	24017.8
$^{12}_{112} - ^{11}_{29}$	23742.3
$^{12}_{211} - ^{11}_{38}$	19321.7
$^{12}_{210} - ^{11}_{39}$	19722.5
$^{13}_{49} - ^{13}_{310}$	21694.1
$^{13}_{212} - ^{12}_{39}$	22194.1
$^{13}_{211} - ^{12}_{310}$	22735.0
$^{14}_{410} - ^{14}_{311}$	21676.1
$^{14}_{213} - ^{13}_{310}$	25052.1
$^{14}_{212} - ^{13}_{311}$	25773.1
$^{15}_{412} - ^{15}_{313}$	21700.7
$^{15}_{411} - ^{15}_{312}$	21651.9
$^{15}_{312} - ^{14}_{411}$	22051.1

Continued

Continuation of Table V
Spectral Assignment of $^{32}\text{SF}_2\text{NCOF}^a$
(MHz)

Transition	Frequency
$16_{412} - 16_{313}$	21621.4
$16_{314} - 15_{411}$	24921.1
$16_{313} - 15_{412}$	24992.3
$17_{413} - 17_{314}$	21585.4
$18_{415} - 18_{316}$	21676.5
$18_{414} - 18_{315}$	21540.7
$19_{416} - 19_{317}$	21669.7
$19_{415} - 19_{316}$	21484.0
$20_{417} - 20_{318}$	21664.7
$20_{416} - 20_{317}$	21419.1
$21_{418} - 21_{319}$	21660.1
$22_{419} - 22_{320}$	21660.1
$23_{420} - 23_{321}$	21664.7
$24_{421} - 24_{322}$	21676.1
$25_{422} - 25_{323}$	21689.3
$27_{424} - 27_{325}$	21740.7
$28_{425} - 28_{326}$	21780.4
$29_{327} - 29_{228}$	18189.5

Continued

Continuation of Table V
Spectral Assignment of $^{32}\text{SF}_2\text{NCOF}$ ^a
(MHz)

Transition	Frequency
$^{29}_{425} - ^{29}_{326}$	20008.1
$^{30}_{427} - ^{30}_{328}$	21889.3
$^{30}_{426} - ^{30}_{327}$	19744.9
$^{31}_{329} - ^{31}_{230}$	18839.0
$^{33}_{331} - ^{33}_{232}$	19567.2
$^{33}_{430} - ^{33}_{331}$	22150.5
$^{34}_{332} - ^{34}_{233}$	19961.1
$^{37}_{434} - ^{37}_{335}$	22731.0
$^{40}_{338} - ^{40}_{239}$	22687.7

a. Measurements believed to be accurate to ± 0.2 MHz.

Table VI
Spectral Assignment of $^{34}\text{SF}_2\text{NCOF}^{\text{a}}$
(MHz)

Transition	Frequency
$6_{16} - 5_{05}$	19985.3
$7_{07} - 6_{06}$	20205.7
$7_{16} - 6_{15}$	20372.9
$7_{26} - 6_{25}$	20226.4
$7_{25} - 6_{24}$	20250.4
$7_{44} - 6_{43}$	20231.3
$7_{17} - 6_{06}$	22736.3
$8_{18} - 7_{17}$	22942.7
$8_{17} - 7_{16}$	23281.2
$8_{27} - 7_{26}$	23115.2
$8_{18} - 7_{07}$	25471.4
$9_{19} - 8_{18}$	25807.8

a. Measurements believed to be accurate to ± 0.3 MHz.

SF_2NCOF , the LRMW spectrum of SF_2NCOF gives support for only one positional isomer, since only one set of R-type bands and only one set of Q-type bands were observed.

Provided the rotational constants of SF_2NCOF are sufficiently sensitive to different orientations about the N=S and N-C bonds, the isomer which supports the observed spectrum can be ascertained by matching the experimental values of B+C and 2A-B-C to those calculated from reasonable models which contain molecular dimensions from molecules related to SF_2NCOF .

An experimental value of $B+C = 2913 \pm 2$ MHz was obtained using a least-squares fit of

$$\nu = (B+C)(J+1)$$

to the experimental peak frequencies of the R-type bands. Because SF_2NCOF has two conformational degrees of freedom, a second rotational parameter, 2A-B-C, must be obtained in order to completely determine its conformation. By fitting the experimental frequencies of the Q-type bands to

$$\nu = (2A-B-C)(K_{-1} + \frac{1}{2})$$

the rotational parameter $2A-B-C = 6230 \pm 20$ MHz was obtained. From the average B+C and the average 2A-B-C, the A rotational constant was determined to be 4572 ± 22 MHz.

To match the above rotational parameters, a meaningful

qualitative structure for N-fluoroformyliminosulfur difluoride was derived by combining the $N=SF_2$ parameters from chloroiminosulfur difluoride,¹⁷ the COF parameters from acetyl fluoride,²⁹ and the N-C distance and the NCO angle from formamide.³⁰ Because no gas-phase value for a SNC angle involving the atom hybridization scheme $sp^3sp^2sp^2$ could be found in the literature, this angle was varied systematically from $110^\circ - 140^\circ$ by 2° increments. Furthermore, the heavy atoms S, N, and C were assumed to lie in a plane which bisects $\angle FSF$. Table VII contains the preliminary structure used in fitting the LRMW spectrum for the purpose of conformational analysis. The plausible positional isomers of SF_2NCOF , which have extreme configurations about the N=S and N-C bonds, are shown in Figure VII. A comparison of the calculated and observed rotational parameters for these isomers is given in Table VIII. The calculated rotational parameters were obtained by directly transferring the geometrical parameters of Table VII to the respective parts of SF_2NCOF and by optimizing the $\angle SNC$ until the best agreement between experiment and theory was achieved.

Although the best agreement between the observed and calculated parameters is obtained for isomer I, isomer II cannot be ruled out entirely based on the low resolution data. Both isomers I and II have a cis configuration

Table VII
 Preliminary Structure of
 N-Fluoroformyliminodulfur Difluoride^a

Structural Parameters	Derived Source	Technique
r(N=S) = 1.476	SF ₂ NCl	Electron Diffraction
r(S-F) = 1.596	"	"
<NSF = 111.2 ^o	"	"
<FSF = 89.8 ^o	"	"
r(C=O) = 1.181	CH ₃ COF	Microwave
r(C-F) = 1.348	"	"
<OCF = 121.35	"	"
r(N-C) = 1.376	H ₂ NCOH	Microwave
<NCO = 123.8	"	"
<SNC = 100 - 130	---	---

a. Bond lengths are in Å and bond angles in degrees.

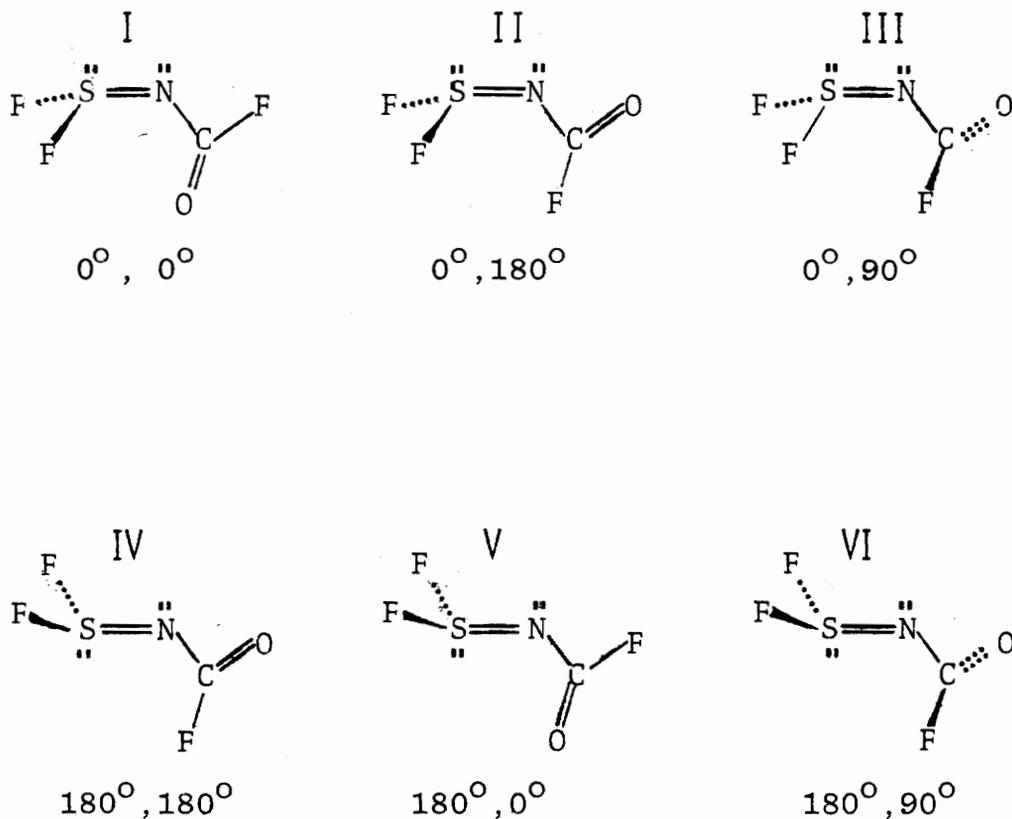


Figure VII. Plausible Positional Isomers of N-Fluoroformyliminosulfur Difluoride^a

^a. The numbers refer to the dihedral angles about the N=S bond and the N-C bond, respectively. The cis configuration about the N=S bond with the conformation about N-C, chosen so that the fluorine atom of the COF group is cis to the lone-pair of electrons on nitrogen, corresponds to $0^\circ, 0^\circ$.

Table VIII

Comparison of Calculated and Observed LRMW Rotational
Parameters of the Normal Isotopic Species of
N-Fluoroformyliminosulfur Difluoride

Isomer	B+C(MHz)	2A-B-C(MHz)	A(MHz)	κ
I	2914	6586	4750	-0.97
II	3208	5758	4483	-0.94
III	3159	4776	3968	-0.79
IV	2477	8067	5272	-1.0
V	2362	8446	5404	-1.0
VI	2456	7720	5088	-0.88
Observed	2913 \pm 2	6230 \pm 20	4572 \pm 22	-0.98 ^a

a. Kappa estimated from linewidth at half-intensity

about the N=S bond and a molecular plane of symmetry, which is the perpendicular bisector of the \angle FSF. However, isomer I has the fluorine atom of the COF group eclipsing the lone pair of electrons on nitrogen, whereas the oxygen atom of the COF group eclipses this lone pair in isomer II. The near coincidence of the inverse moments of these two isomers, which can be attributed to the similarity of the atomic masses of fluorine and oxygen, prevents a firm deduction as to which isomer best fits the spectral data. Analogous ambiguities, due to the similarity of the masses of fluorine and oxygen, were also cited in the conformational studies of propionyl fluoride,³¹ acryloyl fluoride,³² and methyl fluoroformate.³³

Regardless of the indistinguishability of isomers I and II, the rotational constants of isomer III and of all isomers which have a trans conformation about N=S: IV, V, and VI, are very dissimilar to the observed constants, and therefore, are not responsible for the observed spectrum.

C. High Resolution Spectrum and Molecular Structure of N-Fluoroformyliminosulfur Difluoride

The most striking feature of the high resolution microwave spectrum of fluoroforformyliminosulfur difluoride is its richness. Irrespective of the existence of several isomeric forms, three possible factors contributing to the spectral density may be put forth: (1) Large molecules

have small rotational constants which result in closely spaced rotational energy levels, and, therefore, many transitions fall within the accessible microwave region; (2) Flexible molecules have many low-lying vibrational states with significant populations, even at low temperatures, which results in rotational transitions occurring in excited vibrational states; (3) Transitions of the ^{34}S isotopic species, though of low abundance, are also observable.

Although the spectral density is explainable, the presence of so many lines still poses a problem. Routinely, rotational transitions are assigned on the basis of their expected Stark shifts. Because the line density prevented the resolution of the Stark components, this approach was not feasible. Instead, the more difficult process of correlating line positions and line intensities with those predicted from a suitable model was used.

In order to assign a high resolution spectrum it is useful first to calculate the possible range for the experimentally accessible rotational transitions. In the absence of any observable rotational hyperfine structure, only the rotational constants A, B, and C, and the dipole moment components are required for this calculation. Tentative values of the rotational constants can be derived from either a reasonable assumed structure or determined experi-

mentally from the assignment of a low resolution microwave spectrum, provided the spectrum contains a sufficient number of different band types.

Since the low resolution microwave spectrum of the normal isotope of SF_2NCOF contains only bands sensitive to B+C and 2A-B-C, all three rotational constants could not be individually determined. Therefore, the Moment of Inertia computer program, which is described in Appendix A, was used to calculate the rotational constants for the proposed structure (Figure VIII) which best fitted the LRMW spectral data. Transition frequencies and relative line intensities were then calculated by entering these rotational constants and assumed dipole components, $\mu_a = \mu_b = 1.0\text{D}$, into the Asymmetric Rigid Rotor computer program (Appendix A). The rigid rotor spectrum predicted several high intensity ^bQ -branch transitions and ^aR -branch transitions, medium intensity ^bR -branch transitions, and low intensity ^bP -branch transitions. This spectrum also indicated that the ^aR -branch transitions, $J = 7 \leftarrow 6$, $8 \leftarrow 7$, and $10 \leftarrow 9$, should be clustered around the band centers determined from the LRMW spectrum.

First attempts at fitting the spectrum to a rigid rotor model involved the assignment of members of the ^aR -branch, since the low J transitions of this branch are shifted relatively little from their rigid rotor positions.

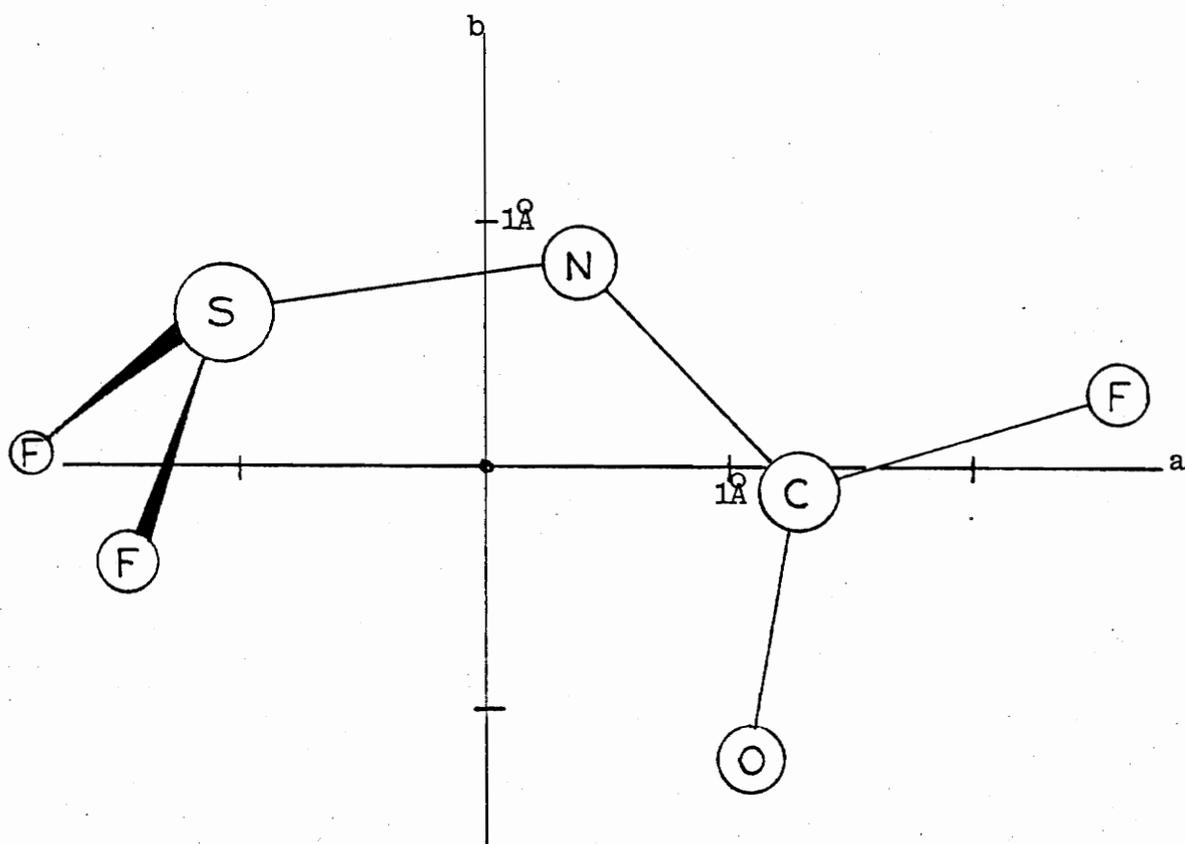


Figure VIII. Proposed Structure of N-Fluoroformyl-iminosulfur Difluoride Based on LRMW Results

Moreover, it was felt that the positions of these transitions were well determined from the assigned LRMW spectrum. Although both the calculated and the experimental spectra indicated that the high K_{-1} components of the aR bands would be very closely spaced, the calculated spectrum did indicate that the $K_{-1}=1$ and $K_{-1}=2$ doublets, and possibly even the $K_{-1}=0$ transitions, would be split out from the band centers and thus resolvable. To a first order approximation, the K_{-1} doublets $(J+1)_{1,J+1} \leftarrow J_{1J}$ of a near prolate asymmetric rotor are separated by $\Delta\nu = (B-C)(J+1)$.³⁴ This splitting factor was helpful in assigning the $K_{-1}=1$ doublets of the $J = 7 \leftarrow 6, 8 \leftarrow 7, \text{ and } 10 \leftarrow 9$ transitions and for obtaining an estimate of $B-C$. To locate the $K_{-1}=0$ transitions, denoted by $J+1_{0,J+1} \leftarrow J_{0J}$, use was made of the fact that the interval of separation between the centers of the closely spaced pair $J+1_{0,J+1} \leftarrow J_{0J}$ and $(J+1)_{1,J+1} \leftarrow J_{1J}$ to the next such pair is $\sim 2C$.³⁵ This approximation aided in the location of the $8_{08} \leftarrow 7_{07}$ and $9_{09} \leftarrow 8_{08}$ transitions.

Since the frequency of the low J aR branch transitions depend primarily upon B and C , they cannot be used to determine the A rotational constant. A value for A must be determined by assigning bR or bQ branch transitions. The assignment of bR transitions of the type $(J+1)_{1,J+1} \leftarrow J_{0J}$ and $(J+1)_{0,J+1} \leftarrow J_{1J}$ was facilitated by using the sum

relationship between a pair of these lines and a pair of previously assigned ^aR-type transitions involving the same four energy levels.³⁶ The sum relationship is

$$\nu\{(J+1)_{0,J+1} \leftarrow J_{0J}\} + \nu\{(J+1)_{1,J+1} \leftarrow J_{1J}\} = \\ \nu\{(J+1)_{1,J+1} \leftarrow J_{0J}\} + \nu\{(J+1)_{0,J+1} \leftarrow J_{1J}\} .$$

This expression, together with the assignment of the $8_{08} - 7_{07}$ and $8_{18} - 7_{17}$ transitions, aided in the assignment of the $8_{18} - 7_{07}$ and $8_{08} - 7_{17}$ transitions.

Because high intensity lines belonging to the Q branch series $J_4 J_{-4} - J_3 J_{-3}$ and $J_4 J_{-3} - J_3 J_{-2}$ prevailed the spectrum and because the assignment of members of this series would afford a better value of A-C and κ , it was desirable to include members of this series in the assignment. Verification of the assignment of a series of Q branch transitions can be facilitated by plotting values of $\frac{A-C}{2}$ as a function of κ .³⁷ To see why this is so, we must consider the general energy level expression for an asymmetric rotor:³

$$E_{J_{K_{-1}K_{+1}}} = \frac{1}{2}(A+C)J(J+1) + \frac{1}{2}(A-C)E(\kappa)$$

where the reduced energy, $E(\kappa)$, is an explicit function of K_{-1} , K_{+1} and κ . The reduced energy also has the property of being symmetric; i.e., $E(\kappa) = E(-\kappa)$.

By an appeal to the selection rule $\Delta J=0$, the frequency of a Q branch transition, obtained from the general energy level expression, is written as:

$$\nu = \frac{1}{2}(A-C)\Delta E(\kappa)$$

where $\Delta E(\kappa)$ is the difference between the reduced energies of the two rotational states involved in the transition. From the above frequency expression it can be seen that if $\frac{A-C}{2}$ is plotted against κ for a family of Q branches, i.e., those transitions having like values of K_{-1} , a curve results for each transition plotted. All Q branch transitions belonging to the same molecule must be associated with a particular value of $\frac{A-C}{2}$ and κ . Therefore, the curves representing correctly assigned transitions will intersect at a common point, namely, $\frac{A-C}{2}, \kappa$. If a common intersection is not achieved, either a wrong J value was assigned to a transition, or, possibly, the transition belongs to another vibrational state.

When performing a Q branch analysis, it is desirable to assign low J transitions so that the effects of centrifugal distortion will be minimal. Although Q branch transitions of low J were present in the 12.0 - 26.4 GHz region, they were not resolvable even under high-resolution conditions. Consequently, transitions involving higher rotational states, namely, J=15-20, had to be used

in the analysis.

Obtaining a graphical estimate of $\frac{A-C}{2}$ and κ by the method described above involves the acquisition of $E(\kappa)$ values as a function of small changes in κ . Tabulated values of $E(\kappa)$ exist in κ increments of 0.01 for $J \leq 12$. However, no such precise tabulation is available for higher rotation states.

Since interpolation of existing tables of $E(\kappa)$ for the higher rotational states is fraught with tedium and inaccuracy, an analytical method³⁸ for calculating the point $\frac{A-C}{2}$, κ was employed. This method determines the reduced energy as a power series expansion of the asymmetry parameter $\delta = \frac{\kappa+1}{2}$. The reduced energy, so expanded, has the form:

$$E(\delta) = a + b\delta + c\delta^2 + d\delta^3 + e\delta^4 .$$

To determine the coefficients of δ in the above expression, a series of $E(\delta)$ and δ values computed by the Rigid Rotor computer program (Appendix A) is least-squares fitted. The derived coefficients are then input to the above power series so that more precise $E(\delta)$ values can be calculated. Once the $E(\delta)$ values have been obtained, the expression for the frequency of a Q branch transition

$$\nu_i = \frac{A-C}{2} (a_i + b_i\delta + c_i\delta^2 + d_i\delta^3 + e_i\delta^4)$$

where $a_i = a_u - a_L$, etc. are the differences between the corresponding coefficients for the two levels involved in the transition, can be used to determine δ values for all pairs of assigned transitions. The δ values are then averaged and the average value is used, along with the experimental frequencies, to compute $\frac{A-C}{2}$. For the normal isotopic species of SF_2NCOF an average value of $\delta = 0.01349 \pm 0.0005$, which corresponds to an average value of $\kappa = 0.9730 \pm 0.0005$, was obtained. This average value of δ when used in the above expression yields an average value of $\frac{A-C}{2} = 1563.09 \pm 0.06$ MHz. Figure IX illustrates a plot of $\frac{A-C}{2}$ as a function of δ for select members of the Q branch series $J_4 J-4 - J_3 J-3$.

Following the initial identification of the Q branch transitions by means of the crossing point analysis, the transitions were incorporated into the spectral fit. However, since these transitions are between higher angular momentum states, their frequencies are more sensitive to the values of the moments of inertia, and are subsequently affected to a greater degree by centrifugal distortion. As a result of the inclusion of the $J=15-20$ transitions into the assignment, the moments of inertia can no longer be considered independent of the rotational state, and a new model, the semirigid rotor, had to be adopted to provide satisfactory spectral predictions.

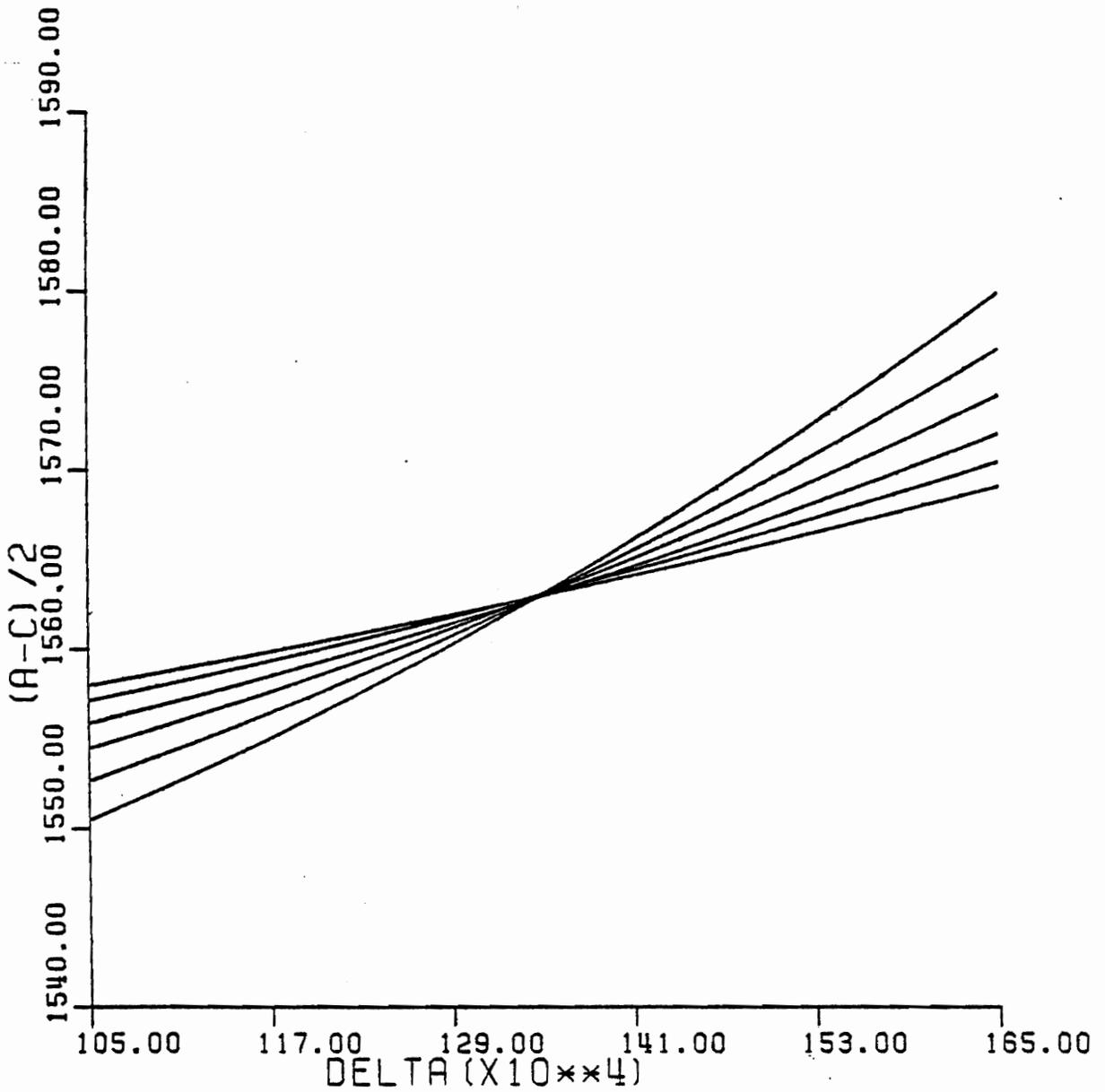


Figure IX. Plot of $\frac{A-C}{2}$ as a Function of Delta for $^{32}\text{SF}_2\text{NCOF}_2$.

The Hamiltonian for the semirigid rotor in the principal axis system may be expressed as³

$$H' = H'_{RR} + H'_{CD} .$$

H'_{RR} is the rigid rotor Hamiltonian with the familiar form

$$H'_{RR} = A'P_a^2 + B'P_b^2 + C'P_c^2$$

where A' , B' , C' are the rotational constants while P_a , etc. are the components of the angular momentum along the molecule-fixed axis in units of \hbar . The distortion Hamiltonian, H'_{CD} , is of the form

$$H'_{CD} = \frac{\hbar^4}{4} \sum_{\alpha, \beta, \gamma, \delta} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta$$

with distortion constants $\tau_{\alpha\beta\gamma\delta}$ and components of the angular momentum P_α , P_β , P_γ , P_δ . The τ 's are functions of the molecular masses, molecular geometry, and force constants. In principal, the distortion constants can be obtained from the force constants, which, in turn, can be determined from the vibrational frequencies. For polyatomic molecules, this is seldom possible because of the involved analysis and the large uncertainties which are attached to any force constants which may emerge. Once a sufficient number of transitions with appreciable distortion effects and different sub-branches have been measured, the rotational constants and the centrifugal distortion

constants can be determined and then used to predict other high J transitions.

To a first order approximation, the eighty-one terms appearing in the distortion Hamiltonian are reduced to six by the Kivelson-Wilson formulation.³⁹ This simplification leads to the following form for the semirigid rotor Hamiltonian

$$\begin{aligned}
 H &= H_{RR} + H_{CD} \\
 H_{RR} &= A' P_a^2 + B' P_b^2 + C' P_c^2 \\
 H_{CD} &= \frac{1}{4} \sum_{\alpha \neq \beta} \tau'_{\alpha\alpha\beta\beta} P_\alpha^2 P_\beta^2
 \end{aligned}$$

where

$$\begin{aligned}
 A' &= A + \frac{\hbar^4}{4} (3\tau_{bcbc} - 2\tau_{baba} - 2\tau_{caca}) \\
 B' &= B + \frac{\hbar^4}{4} (3\tau_{caca} - 2\tau_{bcbc} - 2\tau_{baba}) \\
 C' &= C + \frac{\hbar^4}{4} (3\tau_{baba} - 2\tau_{bcbc} - 2\tau_{caca}) \\
 \tau'_{\alpha\alpha\beta\beta} &= \hbar^4 (\tau_{\alpha\alpha\beta\beta} + 2\tau_{\alpha\beta\alpha\beta}) \\
 \tau'_{\alpha\alpha\alpha\alpha} &= \hbar^4 \tau_{\alpha\alpha\alpha\alpha}
 \end{aligned}$$

with

$$\alpha \neq \beta .$$

Watson,⁴⁰ noting that not all six of the distortion constants within the Kivelson-Wilson model were independent, further reduced the number of centrifugal distortion

constants to five. In terms of Watson's parameters the Hamiltonian is

$$\begin{aligned}
 H = & \frac{1}{2}(\bar{B}+\bar{C})P^2 + [\bar{A} - \frac{1}{2}(\bar{B}+\bar{C})]P_a^2 - \Delta_J(P^2)^2 - \\
 & \Delta_{JK}P^2P_a^2 - \Delta_KP_a^4 + (P_a^2 - P_c^2) \left[\left(\frac{1}{2} \right) (\bar{B}-\bar{C}) - \right. \\
 & \left. \delta_J P^2 - \delta_K P_a^2 \right] + \left[\frac{1}{2}(\bar{B}-\bar{C}) - \delta_J P^2 - \delta_K P_a^2 \right] [P_b^2 - P_c^2]
 \end{aligned}$$

The rotational constants are written as

$$\begin{aligned}
 \bar{A} &= A' + 16R_6 \\
 \bar{B} &= B' + 16R_6 \left(\frac{A'-C'}{B'-C'} \right) \\
 \bar{C} &= C' + 16R_6 \left(\frac{A'-C'}{B'-C'} \right)
 \end{aligned}$$

where $R_6 = \left(\frac{1}{64} \right) \tau_{bbbb} + \tau_{cccc} - 2(\tau_{bbcc} + 2\tau_{bcbc}) \hbar^4$. The following relationships rephrase the τ 's of the Kivelson-Wilson formulations in terms of the Δ 's and δ 's of the Watson model

$$\begin{aligned}
 \Delta_J &= -\frac{1}{8}(\tau'_{bbbb} - \tau'_{cccc}) \\
 \Delta_K &= -\frac{1}{4}(\tau'_{aaaa} + \tau'_{bbbb} + \tau'_{cccc}) + \frac{\tau_1}{4} \\
 \Delta_{JK} &= \frac{3}{8}(\tau'_{bbbb} + \tau'_{cccc}) - \frac{\tau_1}{4} \\
 \delta_J &= -\frac{1}{16}(\tau'_{bbbb} - \tau'_{cccc}) \\
 \delta_K &= \frac{1}{8}\tau'_{bbbb} \left(\frac{B'-A'}{B'-C'} \right) + \frac{1}{8}\tau'_{cccc} \left(\frac{C'-A'}{B'-C'} \right) + \\
 & \quad \frac{\tau_1}{8} \left(\frac{B'+C'}{B'-C'} \right) + \frac{\tau_2}{4} \left(\frac{1}{B'-C'} \right)
 \end{aligned}$$

where

$$\tau_1 = \tau'_{ccaa} + \tau'_{bbaa} + \tau'_{bbcc}$$

and

$$\tau_2 = B'\tau'_{ccaa} + C'\tau'_{bbaa} + A'\tau'_{bbcc}$$

Sixty-five transitions of the normal isotopic species of fluoroformyliminosulfur difluoride were measured and fit to a centrifugal distortion model of the Watson formulation using techniques and an algorithm developed by Kirchhoff.⁴¹ A description of the semirigid rotor program is presented in Appendix A. The results of the distortion fit are given in Table IX, while the spectroscopic constants are listed in Table X. The average and root mean square deviations of the fit are 0.213 MHz and 1.130 MHz, respectively, while the standard deviation is 0.936 MHz.

Since ³⁴S has a natural abundance of approximately 4%, the spectrum of ³⁴SF₂NCOF is observable. Routine techniques used to distinguish absorptions belonging to isotopic species in low natural abundance from those belonging to more abundant isotopes include: (1) Comparison of the intensity of a particular rotational line of the isotopic species to the intensity of the corresponding transition (identical rotational and vibrational states) of the parent species measured at the same temperature; (2) Fre-

Table IX
 Centrifugal Distortion Fit of $^{32}\text{SF}_2\text{NC OF}^a$
 (MHz)

Transition	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$4_{23} - 3_{12}$	20852.5	20852.6	-0.1
$4_{22} - 3_{13}$	21100.9	21100.6	0.3
$5_{24} - 4_{13}$	23685.6	23684.8	0.8
$5_{23} - 4_{14}$	24101.2	24102.3	-1.1
$6_{16} - 5_{05}$	20170.3	20171.3	-1.0
$6_{25} - 5_{14}$	26496.5	26496.8	-0.3
$7_{07} - 6_{06}$	20369.5	20371.9	-2.4
$7_{17} - 6_{16}$	20245.4	20247.4	-2.0
$7_{16} - 6_{15}$	20530.4	20529.5	0.9
$7_{26} - 6_{25}$	20388.9	20389.9	-1.0
$7_{25} - 6_{24}$	20412.3	20412.3	0.0
$7_{17} - 6_{06}$	22954.0	22952.1	1.9
$8_{08} - 7_{07}$	23273.2	23274.4	-1.2
$8_{18} - 7_{17}$	23138.2	23138.1	0.1
$8_{17} - 7_{16}$	23460.3	23460.1	0.2
$8_{27} - 7_{26}$	23302.1	23301.2	0.9
$8_{26} - 7_{25}$	23336.8	23334.8	2.0
$8_{08} - 7_{17}$	20694.6	20694.3	0.3
$8_{18} - 7_{07}$	25718.3	25718.2	0.1

Continued

Continuation of Table IX
Centrifugal Distortion Fit of $^{32}\text{SF}_2\text{NCOF}^a$
(MHz)

Transition	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$^9_{09} - ^8_{08}$	26172.9	26173.9	-1.0
$^9_{19} - ^8_{18}$	26027.8	26027.9	0.1
$^9_{18} - ^8_{17}$	26390.0	26389.8	0.2
$^9_{28} - ^8_{27}$	26210.4	26211.9	-1.5
$^9_{09} - ^8_{18}$	23731.3	23730.2	1.1
$^{11}_{111} - ^{10}_{28}$	21166.3	21167.5	-1.2
$^{11}_{110} - ^{10}_{29}$	24017.8	24019.1	-1.3
$^{12}_{112} - ^{11}_{29}$	23742.3	23742.3	0.0
$^{12}_{211} - ^{11}_{38}$	19321.7	19321.6	0.1
$^{12}_{210} - ^{11}_{39}$	19722.5	19722.5	0.0
$^{13}_{49} - ^{13}_{310}$	21694.1	21694.3	-0.2
$^{13}_{212} - ^{12}_{39}$	22194.1	22192.5	1.6
$^{13}_{211} - ^{12}_{310}$	22735.0	22736.7	-1.7
$^{14}_{410} - ^{14}_{311}$	21676.1	21675.8	0.3
$^{14}_{213} - ^{13}_{310}$	25052.1	25051.4	0.7
$^{14}_{212} - ^{13}_{311}$	25773.1	25772.5	0.6
$^{15}_{412} - ^{15}_{313}$	21700.7	21699.8	0.9
$^{15}_{411} - ^{15}_{312}$	21651.9	21652.3	-0.4
$^{15}_{312} - ^{14}_{411}$	22051.1	22050.8	0.3
$^{16}_{412} - ^{16}_{313}$	21621.4	21622.7	-1.3

Continued

Continuation of Table IX
 Centrifugal Distortion Fit of $^{32}\text{SF}_2\text{NCOF}^a$
 (MHz)

Transition	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$16_{314} - 15_{411}$	24921.1	24920.8	0.3
$16_{313} - 15_{412}$	24992.3	24992.9	-0.6
$17_{413} - 17_{314}$	21585.4	21585.9	-0.5
$18_{415} - 18_{316}$	21676.5	21676.0	0.5
$18_{414} - 18_{315}$	21540.7	21540.4	0.3
$19_{416} - 19_{317}$	21669.7	21669.4	0.3
$19_{415} - 19_{316}$	21484.0	21484.7	-0.7
$20_{417} - 20_{318}$	21664.7	21664.3	0.4
$20_{416} - 20_{317}$	21419.1	21417.4	1.7
$21_{418} - 21_{319}$	21660.1	21661.6	-1.5
$22_{419} - 22_{320}$	21660.1	21661.8	-1.7
$23_{420} - 23_{321}$	21664.7	21666.0	-1.3
$24_{421} - 24_{322}$	21676.1	21675.0	1.1
$25_{422} - 25_{323}$	21689.3	21689.8	-0.5
$27_{424} - 27_{325}$	21740.7	21741.3	-0.6
$28_{425} - 28_{326}$	21780.4	21780.3	-0.1
$29_{327} - 29_{228}$	18189.5	18190.9	-1.4
$29_{425} - 29_{326}$	20008.1	20008.0	0.1
$30_{427} - 30_{328}$	21889.3	21890.5	-1.2

Continued

Continuation of Table IX
 Centrifugal Distortion Fit of $^{32}\text{SF}_2\text{NCOF}^a$
 (MHz)

Transition	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$30_{426} - 30_{327}$	19744.9	19742.6	2.3
$31_{329} - 31_{230}$	18839.0	18839.9	-0.9
$33_{331} - 33_{232}$	19567.2	19569.3	-2.1
$33_{430} - 33_{331}$	22150.5	22153.9	-3.4
$34_{332} - 34_{233}$	19961.1	19963.1	-2.0
$37_{434} - 37_{335}$	22731.0	22733.7	-2.7
$40_{338} - 40_{239}$	22687.7	22688.8	-1.1

a. Observed frequencies believed to be accurate to ± 0.2 MHz. Calculated frequencies based on spectroscopic constants listed in Table X.

Table X
Spectroscopic Constants for $^{32}\text{SF}_2\text{NCOF}$
(MHz)

A	=	4563.584±0.085
B	=	1476.855±0.048
C	=	1436.517±0.043
τ_1	=	-0.0383±0.0036
τ_2	=	-0.008±0.0012
τ_3	=	-3.15±0.25
τ^a_{aaaa}	=	0
τ_{bbbb}	=	0.0036±0.0013
τ_{cccc}	=	0.0035±0.0014
h_J	=	-0.311±0.070 x 10 ⁻⁵
h_{JK}	=	0.132±0.027 x 10 ⁻⁵

- a. τ_{aaaa} was not fit because it is too highly correlated with the A rotational constant.

quency fitting by the least-squares reduction process to the appropriate model describing rotation, e.g., rigid rotor or distortable rotor; (3) Stark effect; (4) Measurement of the temperature dependence of the intensities; (5) rf-Microwave double resonance.

Because of the complexity of the spectrum and the microwave spectrometer system available, all of the aforementioned methods could not be used to identify the transitions of $^{34}\text{SF}_2\text{NCOF}$. As previously discussed, the density of the spectrum and the broad linewidth hindered the assignment of low J lines based on the anticipated Stark shifts. Identification of ^{34}S lines on the basis of the temperature coefficient of the intensities was also precluded because the spectrum at room temperature was too weak to accurately measure. The diffuseness of the spectrum at room temperature is believed to be due to low frequency vibrations, which depopulate the ground state very rapidly as temperature increases. All measurements had to be made at dry ice temperature where absorptions were roughly ten times as strong as those observed at room temperature.

The only availing techniques for locating and confirming the elusive $^{34}\text{SF}_2\text{NCOF}$ transitions were measuring the intensity ratio of the ground state lines, $^{32}\text{S}/^{34}\text{S} \sim 22.5$, and noting how well the transitions determined the rotational Hamiltonian. In consequence, the assignment of

the ^{34}S species proved very difficult. Because only a limited number of lines having the proper characteristics could be identified, only a rigid rotor fit was attempted. The results of the rigid rotor fit of twelve transitions of $^{34}\text{SF}_2\text{NCOF}$ in the ground vibrational state are summarized in Table XI. The average and root mean square deviations are -0.013 MHz and 0.566 MHz, respectively, while the standard deviation is 0.654 MHz. In Table XII, the spectroscopic constants determined from the fit are presented.

In principle, the complete analysis of a rotational spectrum can yield four different types of molecular structures: r_e , r_o , r_s , and $\langle r \rangle$.³ Ideally, one would like to aim for the r_e structure because it characterizes the equilibrium configuration of the molecule – a hypothetical state in which all dynamics, e.g., vibrational motion, are frozen. In actuality, the equilibrium geometry is not directly obtainable from observed rotational constants, even in the ground vibrational state. All observed rotational constants are merely averages over the vibrational motion associated with a particular vibrational level. Therefore, the A_o , B_o , and C_o obtained from the analysis of the ground state spectrum are averages over the zero-point vibrational motions and, as such, do not mirror the equilibrium geometry. However, if sufficient rotational data can be collected for several vibrationally-excited states

Table XI
Rigid Rotor Fit of $^{34}\text{SF}_2\text{NCOF}^{\text{a}}$
(MHz)

Transition	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$
$6_{16} - 5_{05}$	19985.3	19985.3	0.0
$7_{07} - 6_{06}$	20205.7	20205.8	-0.1
$7_{16} - 6_{15}$	20372.9	20372.8	0.1
$7_{26} - 6_{25}$	20226.4	20226.8	-0.4
$7_{25} - 6_{24}$	20250.4	20251.2	-0.8
$7_{44} - 6_{43}$	20231.3	20232.4	-1.1
$7_{17} - 6_{06}$	22736.3	22735.9	0.4
$8_{18} - 7_{17}$	22942.7	22942.0	-0.7
$8_{17} - 7_{16}$	23281.2	23280.8	0.4
$8_{27} - 7_{26}$	23115.2	23114.8	0.4
$8_{18} - 7_{07}$	25471.4	25472.2	-0.8
$9_{19} - 8_{18}$	25807.8	25807.3	0.5

a. Observed frequencies believed to be accurate to ± 0.3 MHz. Calculated frequencies based on spectroscopic constants listed in Table XII.

Table XII
Spectroscopic Constants^a for $^{34}\text{SF}_2\text{NCOF}$
(MHz)

$$A = 4526.27 \pm 0.99$$

$$B = 1466.229 \pm 0.040$$

$$C = 1423.795 \pm 0.035$$

- a. No centrifugal distortions constants were determined due to the paucity of assigned transitions.

of all the fundamental vibrational modes, relationships which correlate the observed rotational constants to the equilibrium rotational constants can be used to correct for vibrational motion. This correction allows one to approach the r_e structure by extrapolation to the equilibrium state. Although the r_e structure has been derived for several hundred diatomic molecules, an r_e structure for polyatomic molecules is rarely determinable. Attempting an r_e structure for complex molecules, which have numerous vibrational fundamentals, has not met with much success because of two inherent problems: (1) The Boltzmann factor will be small for the high frequency normal modes and, therefore, the weak microwave spectra of the vibrational satellites of these modes will be correspondingly more difficult to detect; (2) Obtaining a convincing assignment of every normal mode in a polyatomic system is an arduous, and often impossible, task.

The simplest type of structure to be considered is the effective structure, r_0 , which represents the average structure over the ground vibrational state. For a diatomic molecule, the effective bond distance r_0 is

$$r_0 = \left(\frac{h}{8\pi^2 \mu B_0} \right)^{\frac{1}{2}} .$$

One serious drawback of the r_0 structure is that it is not isotopic invariant; that is, different isotopic species

yield slightly different values for the bond lengths and bond angles. Thus, only by making the assumption that r_o is identical for each isotopic species can the set of moment equation be used to determine a unique r_o structure. This assumption is more valid for the isotopic substitution of a heavy atom than a light one.

The best compromise, when an r_e structure is not feasible, is to use Costain's method,⁴² which employs equations developed by Kraitchman,⁴³ to determine the substitution structure, r_s . This procedure allows the coordinates of each atom to be determined independently from the isotopic shifts in the moments of inertia which occur as each atom is substituted. A complete r_s structure requires a single substitution at each atom. When this is possible, the isotopic information can be combined through the Kraitchman equations to cancel much of the ambiguities of the atom's position resulting from zero-point vibration effects. Costain has shown that the mean of the r_e and r_o bond lengths closely approximates the r_s bond length, that is,

$$r_s \approx \frac{1}{2}(r_o + r_e) .$$

The r_s structure is believed to provide more consistent sets of structure data than the r_o structure.

The last structure to be dealt with is the average

structure, $\langle r \rangle$. The $\langle r \rangle$ structure represents the molecular configuration for which the nuclear positions have been averaged over the vibrational motion. In contrast to the r_e determination, the complete form of the vibrational potential function, which includes both a harmonic and an anharmonic part, need not be known for a $\langle r \rangle$ solution. Only the exact form of the harmonic part, which can be obtained from the force constants, is needed. Average structures have been determined for numerous diatomics, some linear and nonlinear triatomics, and for a few tetrahedral molecules.

Vibrational motion also makes a significant contribution to the value of the inertia defect. Consideration of the inertia defect can be of great import for demonstration of planarity or molecular planes of symmetry. For a rigid molecule the relation³

$$I_{\alpha} - I_{\beta} - I_{\gamma} = -2P_{\gamma}$$

where

$$\begin{array}{l} I_{\alpha}, I_{\beta} = \text{in-plane moment of inertia} \\ I_{\gamma} = \text{out-of-plane moment of inertia} \\ P_{\gamma} = \text{out-of-plane second moment} \end{array}$$

holds exactly. In the case of a rigid planar molecule, both sides of the above equation vanish. However, experiment has shown that $I_{\alpha} - I_{\beta} - I_{\gamma}$ for a real planar mole-

cule never quite vanishes, but has a small positive value of approximately $0.05 - 0.5 \text{ amu} \cdot \text{Å}^2$, which is termed the inertia defect, Δ . In the ground vibrational state, the inertia defect of a planar molecule is given as

$$\Delta^0 = I_{\alpha}^0 - I_{\beta}^0 - I_{\gamma}^0$$

where, $P_{\gamma}^0 = 0$ obviously follows from the definition of planarity. The analogous expression for a nonplanar molecule with an $\alpha\beta$ plane of symmetry is

$$\Delta^0 = I_{\alpha}^0 - I_{\beta}^0 - I_{\gamma}^0 + 2P_{\gamma}^0$$

where

$$P_{\gamma} = \sum_i m_i \gamma_i^2 \neq 0$$

m_i = mass of i th out-of-plane atom

γ_i = perpendicular distance of i th atom from the $\alpha\beta$ plane

Provided SF_2NCOF possesses an ab plane of symmetry with the only out-of-plane atoms being two symmetrically equivalent fluorines, the above equation can be recast in terms of the out-of-plane coordinate, C_F of the fluorines, yielding

$$\Delta^0 = I_a^0 - I_b^0 - I_c^0 - 4M_F C_F^2 .$$

Because Δ^0 is very small compared to moments of inertia or to the out-of-plane contribution to the inertia, it may, to a first approximation, be safely neglected. This allows

the C coordinate of the fluorines to be calculated directly from the experimentally determined moments of inertia and the relation $C_F = \left(\frac{I_a^0 + I_b^0 - I_c^0}{4M_F} \right)^{\frac{1}{2}}$ giving, $C_F = \pm 1.154 \pm 0.001 \text{ \AA}$ and $C_F = \pm 1.155 \pm 0.002 \text{ \AA}$ respectively, for $^{32}\text{SF}_2\text{NCOF}$ and $^{34}\text{SF}_2\text{NCOF}$. Inasmuch as Δ^0 can be assumed equal for the two isotopic species, the values of C_F can be averaged, yielding $\bar{C}_F = \pm 1.154 \pm 0.003 \text{ \AA}$.

Information pertaining to the conformation of SF_2NCOF can be obtained by noting the similarity of the values of $I_a^0 + I_b^0 - I_c^0$ for the two isotopic species: $I_a^0 + I_b^0 - I_c^0 = 101.13 \pm 0.05 \text{ amu}\cdot\text{\AA}^2$ for $^{32}\text{SF}_2\text{NCOF}$ as compared to $101.38 \pm 0.20 \text{ amu}\cdot\text{\AA}^2$ for $^{34}\text{SF}_2\text{NCOF}$. From this it can be concluded that SF_2NCOF has a plane of symmetry containing the S, N, C, and O atoms and the a and b principle axes. Thus conformers III and VI of Figure VII can be ruled out.

Additionally, the r_s coordinates of the S atom in SF_2NCOF can be computed directly from the observed isotopic shifts in the moments of inertia by utilization of the Kraitchman equations.³ For an asymmetric top, such as SF_2NCOF , the coordinate computation will be more straightforward if the planar dyadic, termed the P tensor, is used instead of the inertia dyadic or \underline{I} tensor. In the center-of-mass principle axis system a_i, b_i, c_i , the \underline{P} tensor is

$$\underline{P} = \begin{vmatrix} P_{aa} & P_{ab} & P_{ac} \\ P_{ba} & P_{bb} & P_{bc} \\ P_{ca} & P_{cb} & P_{cc} \end{vmatrix}$$

with diagonal elements

$$P_{aa} = \sum m_i a_i^2, \text{ etc.}$$

and off-diagonal elements

$$P_{ab} = \sum m_i a_i b_i, \text{ etc.}$$

The planar dyadic is related to the inertia dyadic

$$\underline{I} = \begin{vmatrix} I_{aa} & I_{ab} & I_{ac} \\ I_{ba} & I_{bb} & I_{bc} \\ I_{ca} & I_{cb} & I_{cc} \end{vmatrix}$$

by

$$\underline{P} = d\underline{E} + \underline{I}$$

where

$$d = \sum m_i (a_i^2 + b_i^2 + c_i^2)$$

and

$$\underline{E} = \begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{vmatrix} .$$

The diagonal elements of the \underline{I} tensor, termed the moments of inertia, are

$$I_{aa} = \sum_i m_i a_i^2, \text{ etc.}$$

while the off-diagonal elements or products of inertia are

$$I_{ab} = -\sum_i m_i a_i b_i, \text{ etc. .}$$

From the above definitions, it follows that the diagonal elements of the \underline{P} tensor or planar second moments are equal to the moments of inertia, whereas, the off-diagonal elements of \underline{P} are equal, but of opposite sign, to the products of inertia. Several expressions relating the P's and the I's may be put forth, such as,

$$P_a = \frac{1}{2}(-I_a + I_b + I_c)$$

etc., and

$$I_a = P_a + P_b, \text{ etc. .}$$

Allowing the unprimed quantities to be associated with the parent species, and the primed quantities to denote those of the isotopic species, the r_s coordinates of the relevant atom become

$$|a| = \mu^{-\frac{1}{2}} \left[(P'_{aa} - P_{aa}) \left(1 + \frac{P'_{bb} - P_{bb}}{P_{bb} - P_{aa}} \right) \left(1 + \frac{P'_{cc} - P_{cc}}{P_{cc} - P_{aa}} \right) \right]^{\frac{1}{2}}$$

$$|b| = \mu^{-\frac{1}{2}} \left[(P'_{bb} - P_{bb}) \left(1 + \frac{P'_{cc} - P_{cc}}{P_{cc} - P_{bb}} \right) \left(1 + \frac{P'_{aa} - P_{aa}}{P_{aa} - P_{cc}} \right) \right]^{\frac{1}{2}}$$

$$|c| = \mu^{-\frac{1}{2}} \left[(P'_{cc} - P_{cc}) \left(1 + \frac{P'_{aa} - P_{aa}}{P_{aa} - P_{cc}} \right) \left(1 + \frac{P'_{bb} - P_{bb}}{P_{bb} - P_{aa}} \right) \right]^{\frac{1}{2}}$$

where the reduced mass for isotopic substitution, in terms of the parent species M and the mass shift, is

$$\mu = \frac{M\Delta m}{M + \Delta m} .$$

Insofar as N-fluoroformyliminosulfur difluoride can be considered rigid, i.e., bond distances and bond angles are invariant to isotopic substitution, utilization of the above equations yields, for the r_s coordinates of S

$$|a| = 1.09 \pm 0.01 \text{ \AA}$$

$$|b| = 0.630 \pm 0.006 \text{ \AA}$$

with the following imposed conditions

1. Coordinates a_i , b_i , c_i are measured from the COM principal axes system of the parent species (chosen to be $^{32}\text{SF}_2\text{NCOF}$ in this case)
2. Only the S atom is substituted .

A complete r_s structure for SF_2NCOF , though desired, could not be determined in this investigation. There is only one stable isotope of fluorine and the spectrometer is not sensitive enough to detect the spectrum of the $^{13}C(1.1\%)$, $^{18}O(0.2\%)$, and $^{15}N(0.4\%)$ variants in their natural abundance.

In Table XIII, a summary of the coordinate computations, the F-F nonbonded distance, as well as the criterion which established a heavy-atom plane of symmetry, is presented. All uncertainty limits reflect the estimated experimental uncertainties in A, B, and C.

In the preliminary stages of this investigation six plausible isomers, which are illustrated in Figure VII, were used to fit the LRMW spectra data. All isomers, except isomers I and II, were eliminated on the basis of the LRMW rotational constants (see Table VIII). Moreover, isomers III and IV, which do not contain a plane of symmetry, were also eliminated by the results listed in Table XIII. However, an unequivocal statement as to which of the remaining isomers, I or II, is responsible for the LRMW spectrum or which one is most consistent with the high resolution spectral data is still not determined at this point. Both isomers I and II have a molecular plane of symmetry containing the a and b principal axes and a cis configuration about the N=S bond. In isomer I, the fluorine of the COF group eclipses the lone pair of electrons

Table XIII
 Kraitchman Coordinates of Sulfur,^a
 c Coordinate of Fluorine, Planar Second Moments,
 and F-F Non-bonded Distance for SF₂NCOF^b

a S	1.09 ± 0.01 Å
b S	0.630 ± 0.006 Å
\bar{c}_F	1.554 ± 0.003 Å
.	
I _a + I _b - I _c	101.13 ± 0.05 amu·Å ² ^c
	101.38 ± 0.20 amu·Å ² ^d
F . . . F _{avg}	2.308 ± 0.006 Å

- a. Only absolute values obtained from Kraitchman equations, the sign being indeterminate
- b. Uncertainty limits reflect estimated experimental error in A, B, and C.
- c. For ³²SF₂NCOF
- d. For ³⁴SF₂NCOF.

on nitrogen, whereas, the oxygen eclipses this lone pair in isomer II. Obtaining an unambiguous conformation requires the determination of the structural parameters for both isomers from the high resolution spectroscopic constants. If the set of structural parameters determined from the moments of inertia is found to be unreasonable for one of the isomers, that isomer may be ruled out. An unreasonable set of structural parameters would be parameters found to be substantially different from those of related molecules, such as, SF_2NCl , SF_2NCF_3 , SOF_2 , etc. This procedure was also used to assess the conformation of $\text{SF}_2\text{ONH}^{44}$ from its microwave spectrum.

The molecular structure of N-fluoroformyliminosulfur difluoride which is most reasonable relative to parameters observed in similar molecules and which reproduces the experimentally determined moments of inertia was obtained using the structural fitting computer program, STRFTQ, developed by Schwendeman.⁴⁵ The STRFTQ program adjusts internal coordinates, i.e., bond distances and bond angles, to fit the observed moments of inertia by a least-squares reduction scheme. A more detailed description of this program is presented in Appendix A.

Having previously established a plane of symmetry, ten independent parameters, $r(\text{N}=\text{S})$, $r(\text{N}-\text{C})$, $r(\text{S}-\text{F})$, $r(\text{C}=\text{O})$, $r(\text{C}-\text{F})$, $\angle\text{OCF}$, $\angle\text{NCO}$, $\angle\text{FSF}$, $\angle\text{NSF}$, $\angle\text{SNC}$, and two dihedral

angles must be determined to obtain a complete r_0 structure. For each unknown independent parameter sought, at least one independent moment of inertia is required. Therefore, a minimum of twelve moments of inertia is needed for a complete r_0 structural analysis of SF_2NCOF . Clearly, the six independent moments of inertia obtained from the assignment of only two isotopic species are insufficient for a complete least squares r_0 structure. Several assumptions were necessary to establish a consistent structure from the limited data presently available. The bonding parameters used for the $-COF$ fragment, $r(C=O) = 1.181 \text{ \AA}$, $r(C-F) = 1.348 \text{ \AA}$, and $\angle COF = 121.35^\circ$, were those found for this fragment in a detailed study of acetyl fluoride.²⁹ Additionally, the $\angle NCO$ was assumed to be the same as that determined for formamide.³⁰ The remaining structural parameters, $r(N=S)$, $r(N-C)$, $r(S-F)$, $\angle FSF$, and $\angle NSF$ were evaluated as a function of the angle SNC using the STRFTQ program. The strategy of this program involves fitting the unknown structural parameters to the principal moments of inertia in the ground vibrational state:

$$I_a^0 = \sum m_i a_i^2, \quad I_b^0 = \sum m_i b_i^2, \quad \text{and} \quad I_c^0 = \sum m_i c_i^2.$$

Since the STRFTQ program adjusts internal coordinates, the nontrivial center of mass conditions, $\sum m_i a_i = 0$, $\sum m_i b_i = 0$, and the nontrivial product of inertia conditions, $\sum m_i a_i b_i = 0$, are satisfied automatically, and thus do not have to be in-

cluded in the fitting procedure.

The results of fitting the moments to possible structures indicated that isomer I is more plausible than isomer II. For isomer I, any assumed value for the $\angle\text{SNC}$ from 110° to 140° predicated a structure which contained some bonding parameters which were vastly different from those of related molecules. In contrast, when the $\angle\text{SNC} = 124^\circ$, all of the bonding parameters determined for isomer I were in close agreement with those observed for other iminosulfur difluoride molecules. The refined structure for isomer I is presented in Table XIV and illustrated in Figure X. The quoted uncertainty limits reflect the estimated experimental uncertainties in the moments of inertia. A comparison of the experimental moments of inertia and those calculated from the refined structure is given in Table XV. The root-mean-square deviation of the moments fitted was $0.04 \text{ amu}\cdot\text{\AA}^2$. Because several of the bonding parameters had to be assumed due to a lack of extensive isotopic substitution, the reported structure is not irrefutable. It is felt, however, that since a reasonable structure was not obtained for isomer II, this isomer does not represent the conformation of SF_2NCOF .

Table XIV
Refined Structural Parameters of
N-Fluoroformyliminosulfur Difluoride^a

r_{NS}	$= 1.474 \pm 0.005^{\text{b}}$
r_{CN}	$= 1.448 \pm 0.005$
r_{SF}	$= 1.606 \pm 0.002$
r_{CO}	$= (1.181)^{\text{c}}$
r_{CF}	$= (1.348)$
$\angle \text{SNC}$	$= 124 \pm 1$
$\angle \text{NSF}$	$= 108.6 \pm 0.3$
$\angle \text{FSF}$	$= 91.7 \pm 0.2$
$\angle \text{OCF}$	$= (121.35)$
$\angle \text{NCO}$	$= (123.80)$

- a. Bond lengths in Å, angles in degrees.
- b. Uncertainty limits reflect estimated experimental error in A, B, and C.
- c. Assumed value, see text.

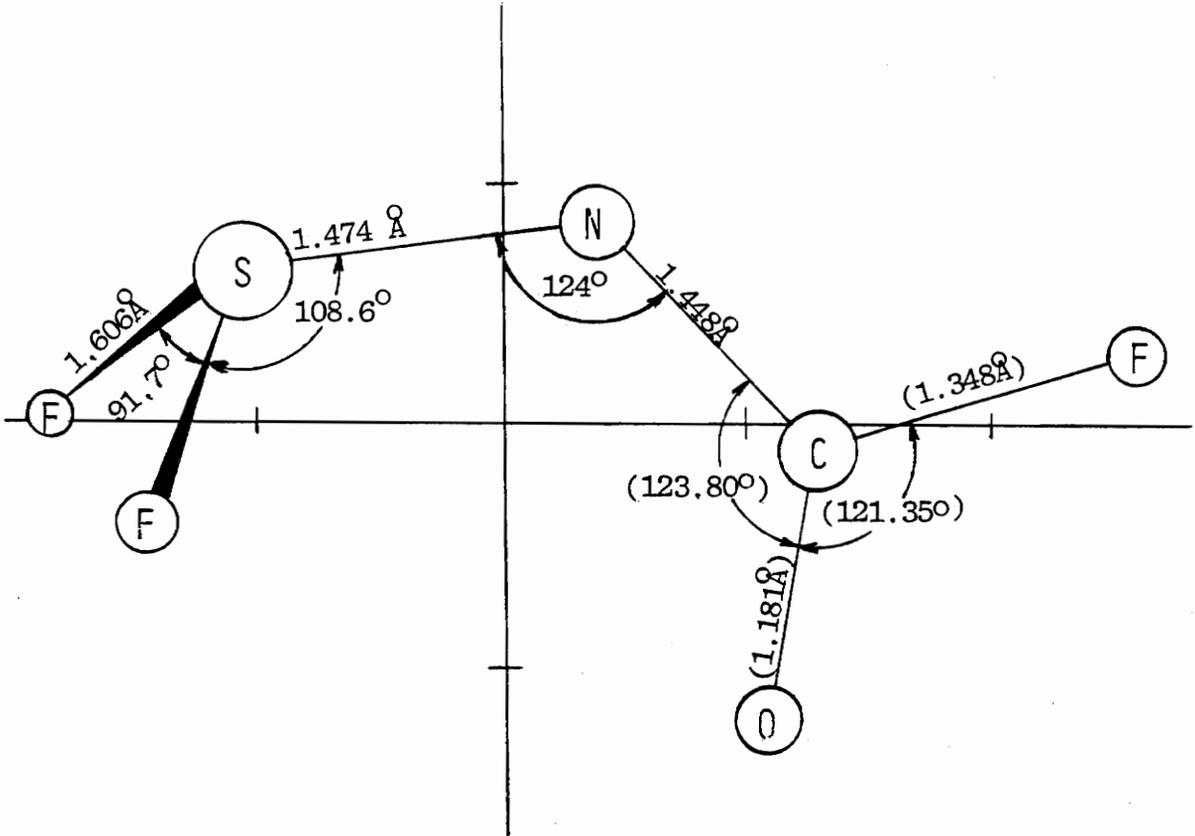


Figure X. Refined Molecular Structure of N-Fluoroformyliminosulfur Difluoride.

Table XV

Comparison of Observed and Calculated Moments of Inertia
for N-Fluoroformyliminosulfur Difluoride
(amu · Å²)

Isotopic Species	Observed Moment	Calculated Moment	O-C
³² SF ₂ NCOF	110.741 ± 0.002 ^a	110.83	-0.09
	342.19 ± 0.01	342.22	-0.03
	351.81 ± 0.01	351.77	0.04
³⁴ SF ₂ NCOF	111.65 ± 0.02	111.57	0.08
	344.68 ± 0.01	344.65	0.03
	354.95 ± 0.01	354.96	-0.01

a. One standard error.

D. Discussion

The low resolution microwave spectrum of N-fluoroformyliminosulfur difluoride, which displayed only one set of R-type bands and one set of Q-type bands, indicated the presence of only one predominant low-energy form of this molecule in the gas phase. Analysis of the LRMW spectrum to determine which isomer(s) gave rise to the observed spectrum was performed by matching the low resolution spectral data with that calculated from models for several orientations of the SF₂ group relative to the N=S bond and for different orientations of COF group about the N-C bond. The calculated asymmetry of the six isomers considered indicated that they are all near prolate rotors with $\kappa \leq -0.7$ and thus capable of exhibiting band spectra. Consequently, none of the plausible isomers could be excluded by this criterion. However, the calculated B+C and 2A-B-C of four of the isomers were quite dissimilar from that observed and were therefore subsequently eliminated. The discarded isomers included two which had a trans configuration about the N=S bond, with an ac plane of symmetry containing the S, N, C, and O atoms, but differing by a 180° rotation of the COF unit. Also eliminated were two isomeric forms which do not contain a molecular plane of symmetry. The calculated LRMW rotational parameters of the remaining two isomers were very

similar and were in close agreement with those observed. These two contending isomers have a cis configuration about the N=S bond and an ab plane of symmetry containing the S, N, C, and O atoms, but differing by a 180° rotation of the carbonyl fluoride group. The difficulty in distinguishing between these two isomers lies in the similarity of the masses of oxygen and fluorine, which, in turn, results in the moments of inertia being rendered relatively insensitive to different orientations of the COF group. The calculation of B+C and 2A-B-C did show, however, that these two isomeric forms should have given resolvable band spectra if they had had comparable line strengths and had been present in comparable concentrations. Because two distinct band spectra were not observed, it can be concluded that either the second isomer represents a high energy form of SF₂NCOF or it has a very small dipole moment.

The establishment of only one predominant isomer of SF₂NCOF, which has a cis conformation about the N=S bond, is in agreement with the conformational studies performed on related molecules. Related molecules would be those molecules having an sp³ hybridized sulfur with a lone pair of electrons occupying one of the hybridized orbitals, and an sp² hybridized nitrogen with one lone pair of electrons occupying one of the hybridized orbitals. Molecules of

the type $X-N=S=O$ and $F_2S=NX$ fall into the above-mentioned bonding scheme. The microwave spectra of $HNSO$,⁴⁶ CH_3NSO ,⁴⁷ $\emptyset NSO$,⁴⁸ and SF_2NSF_5 (this work) were assigned to those species having a cis configuration about $N=S$. Electron diffraction studies of $ClNSO$,⁴⁹ SF_2NCl ,¹⁷ and SF_2NCF_3 ²⁰ also revealed that the conformation about $N=S$ in these molecules is preferentially cis.

A check on the consistency of the assigned spectrum of the normal isotopic species of N-fluoroformylimino-sulfur difluoride can be made using a comparison of the results obtained from the $\frac{A-C}{2}$ vs. δ crossing point analysis (which employs a rigid rotor formulation) with the corresponding results obtained from the nonlinear least-squares centrifugal distortion fit. The values of the rotational constants for $^{32}SF_2NCOF$ based on the centrifugal distortion fit are $A = 4563.584 \pm 0.085$ MHz, $B = 1476.855 \pm 0.048$ MHz, and $C = 1436.517 \pm 0.043$ MHz. The value of $\frac{A-C}{2}$ determined from these constants is 1563 ± 0.08 MHz. The analytically determined crossing point of $\frac{A-C}{2}$ as a function of δ yielded $\frac{A-C}{2} = 1563.09 \pm 0.06$ MHz. The agreement between the values of $\frac{A-C}{2}$ obtained by the two methods is quite reasonable. A value of $\kappa = -0.9730 \pm 0.0005$ was obtained from the crossing point analysis. This value compares reasonably well with $\kappa = -0.9742 \pm 0.0001$ obtained from the centrifugal distortion fit.

Another criterion which can be used to test the validity of an assignment is how well a partial assignment predicts transitions which have not been included in the fit. In the earlier stages of the spectral assignment of $^{32}\text{SF}_2\text{NCOF}$, several low J transitions with $J < 10$ were successfully assigned to a rigid rotor model. Using the newly refined values of the rotational constants from the rigid rotor fit and the quartic centrifugal distortion constants, the $J=15-20$ transitions of the Q-branch series $J_{4,J-4} - J_{3,J-3}$, which were located by the crossing point analysis, were successfully incorporated in the fit. At this point, additional ^bR transitions of $J=10-16$ and ^bQ transitions of $J=20-30$ could be identified and included in the fit. Continuing this 'bootstrapping' approach allowed the assignment of transitions in levels up to J equal to forty. Near a J equal to thirty, the inclusion of two sextic centrifugal distortion constants was deemed necessary to obtain an adequate agreement between experiment and calculation.

In Table XVI, a comparison of the high resolution and low resolution spectral parameters is given. That the values of the high resolution spectral parameters fall within the experimental uncertainty limits of their respective low resolution values is noteworthy.

Several lines which had the correct intensities expected for transitions due to $^{34}\text{SF}_2\text{NCOF}$ in low J states

Table XVI
 Comparison of the High and Low Resolution Microwave
 Rotational Constants for $^{32}\text{SF}_2\text{NCOF}$

	HRMW	LRMW
A	4563.584±0.085 MHz	4572±22 MHz
B	1476.855±0.048 MHz	a
C	1436.517±0.043 MHz	a
κ	0.9744	-0.98 ^b
B+C	2913.37±0.091 MHz	2913± 2 MHz
2A-B-C	6213.80±0.18 MHz	6230±20 MHz

a. Cannot be determined from the LRMW spectral data

b. Kappa estimated from band width at half-intensity

were measured and fit to a rigid rotor model. Although the fit is consistent, it was not used to locate higher J transitions. The difficulty lies in distinguishing between lines belonging to the ^{34}S species and those of vibrationally excited states of the normal isotopic species. As previously mentioned, rf-microwave double resonance would aid in verification and assignment of additional transitions.

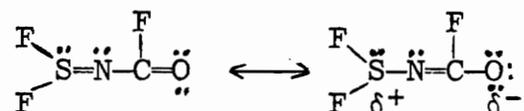
To date, information pertaining to the height of the barrier to rotation about the N=S linkage in iminosulfur difluoride molecules is of a rather inchoate nature. As mentioned briefly in Chapter II, however, some ^{19}F -NMR experiments and some theoretical studies, which should shed some light on the barrier height in these molecules, have been performed. Rotational barriers about the N=S bond of 5.02 - 55.18 kcal/mole were calculated by Shanzer,²⁵ using a CNDO molecular orbital calculation, for various SF_2NR systems (R=F, CF_3 , SF_5 , COF, COCH_3 , and C_6H_5). The barrier height obtained for SF_2NCOF was 13.57 kcal/mole. The observed trend in barrier height $\text{R} = \text{F} < \text{CF}_3 < \text{SF}_5 < \text{COF} < \text{COCH}_3 < \text{C}_6\text{H}_5$, was interpreted on the basis of steric interaction with the recognition that the barrier height observed for $\text{SF}_2\text{N}=\text{SF}_5$ was slightly out of line with this interpretation. The relatively high maxima reported for the iminosulfur difluorides seem to suggest that there is

a hinderance to complete rotation about the N=S linkage. However, since the calculated total energy curve contained two equal minima lying 120 degrees apart and separated by a low lying maximum, Shanzer²⁵ contends that the N=S bond should be considered flexible within this 120 degree interval. Furthermore, Shanzer²⁵ states that the two minima represent two stable isomeric forms of equal energy for the iminosulfur difluorides. This interpretation seems to be in disagreement with the infrared absorption and electron diffraction results on SF₂NCF₃^{19,20} and SF₂NCl,^{18,17} as well as the present low resolution microwave studies on SF₂NCOF and SF₂NSF₅.

The temperature dependence of the ¹⁹F-NMR spectrum of SF₂NCOF was also cited by Shanzer²⁵ as evidence of rotation about the N=S bond. At room temperature, the spectrum consisted of two singlets centered at -118.2 ppm and -96.7 ppm with a relative intensity of 2:1. These singlets were assigned to the SF₂ and NCOF fluorines, respectively. The spectrum was devoid of any fine structure. As low temperatures were approached (~ -80°C), the fluorine resonance of the SF₂ group split into a doublet, while the fluorine resonance of the COF group became a triplet. Biermann and Glemser⁵⁰ also report a temperature-dependent spectrum for SF₂NCOF. However, they proposed no interpretation as to the origin of the observed dependency. The room temperature

^{19}F -NMR spectrum of methyliminosulfur difluoride, CH_3NSF_2 , observed by Cohen and MacDiarmid,⁵¹ which also consisted of a single broad resonance for the SF_2 fluorines and was devoid of any fine structure, was described as due to restricted rotation of the SF_2 group at the $\text{N}=\text{S}$ linkage, rather than as due to free rotation.

Since the $\text{N}-\text{C}$ torsional excited state microwave spectrum was not assigned and a far infrared study has not been performed, very little can be said concerning the nature and the height of the barrier to rotation about the nitrogen-carbon bond in SF_2NCOF . Using a CNDO molecular orbital calculation, Shanzer²⁵ found that there should be little steric restriction to rotation about the $\text{N}-\text{C}$ bond. This, however, does not preclude a barrier to rotation originating from partial double character, acquired through resonance structures of the form



It is well established that rotational barriers between isomeric forms involving rotation about a single bond which has acquired some partial double bond character due to resonance or conjugation is much higher than barriers between normal rotational isomers.⁹

Using the Schomaker-Stevenson rule⁵² as modified by Gordy,⁵³ along with electronegativities,⁵⁴ and covalent

radii,³ the expected lengths of a nitrogen-carbon single bond and a nitrogen-carbon double bond are approximately 1.47 and 1.25 Å, respectively. The refined N-C bond length of 1.448 Å obtained in this study possibly indicates some partial double bond character. However, since the length of the carbonyl bond had to be assumed, the derived N-C length cannot unambiguously confirm the presence of nitrogen-carbon partial double bond character.

If the nitrogen-carbon bond does indeed possess some double bond character, two isomeric forms, such as isomers I and II, which differ by a 180° rotation about the N-C bond, would be expected. Nonetheless, extensive microwave investigations of several conjugated systems including butadiene,⁹ fluoroprene,⁵⁵ isoprene,⁵⁶ acrolein,⁵⁷ crotonaldehyde,⁹ and methyl vinyl ketone,⁵⁸ as well as this work have failed to find evidence of a second isomeric form.

A comparison of the refined structure of SF₂NCOF with that of related molecules is given in Table XVII. Glemser^{61,62} has observed that the N=S bond length in molecules of the type F₂S=N-R, where R is an organic or inorganic ligand, is shorter than the value of 1.53 Å calculated on the basis of the Schomaker-Stevenson rule as modified by Gordy to include double bonds. According to Glemser, this effect, as well as the high value of the stretching frequency of the N=S bond, can be explained by the reson-

Table XVII

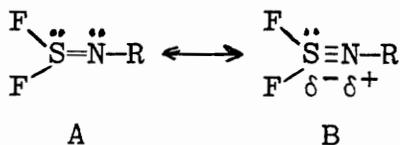
Comparison of the Refined Structural Parameters
of the $\text{N}=\text{SF}_2$ Group of SF_2NCOF with those
of Related Molecules^a

	$r_{\text{N}=\text{S}}$	r_{SF}	$\angle \text{NSF}$	$\angle \text{FSF}$	$\angle \text{SNX}$
$\text{SF}_2\text{NCOF}^{\text{b}}$	1.474	1.608	108.6	92.7	124
NSF_3^{15}	1.416	1.552		94.0	
NSF^{16}	1.448	1.643	116.9		
$\text{SF}_2\text{NCF}_3^{20}$	1.447	1.583	112.6	81.1	130.4
$\text{SF}_2\text{ONH}^{44}$	1.466	1.549	112.9	93.7	115.5
$\text{SF}_2\text{NCl}^{17}$	1.476	1.596	111.2	92.6	120.0
$\text{SF}_2\text{ONCl}^{59}$	1.484	1.548	111.8	92.6	114.7
SOF_2^{60}		1.585		92.8	

a. Bond lengths are in Å, bond angles in degs.

b. This work.

ance forms 13,63



where canonical structure B is assigned more weight than structure A. The N=S bond length found for SF₂NCOF is consistent with the above reasoning as is the value of $\nu_{\text{NS}} = 1350 \text{ cm}^{-1}$.⁴⁷

A linear relationship between the N=S bond length and bond order has also been observed by Glemser.^{14,62} In Table XVIII, a comparison of nitrogen-sulfur bond lengths and bond orders is presented. By interpolation, the bond order of SF₂NCOF is ~ 2.1 .

A further relationship between the force constant, f_{NS} , and bond length, r_{NS} , which is represented by the equation

$$f_{\text{NS}} = 145 r_{\text{NS}}^{-7.0}$$

has been established by Glemser.^{61,64} The force constant calculated from this equation for the N=S bond in SF₂NCOF is $9.6 \text{ mdyne } \text{\AA}^{-1}$. Assuming independent oscillators, a stretching force constant of $10.0 \text{ mdyne } \text{\AA}^{-1}$ is obtained from the ir stretching frequency of 1350 cm^{-1} .

Although this investigation has shown that isomer I is the stable form of N-fluoroformyliminosulfur difluoride

Table XVIII

Some Observed Nitrogen-Sulfur Bond Lengths, r_{NS} ,
and Nitrogen-Sulfur Bond Orders, n_{NS} ^{13,61,62,63,64}

Molecule	r_{NS} , Å	n_{NS}
NSF ₃	1.416	2.7
NSF	1.448	2.4
SF ₂ NCF ₃	1.447	(2.4)
SF ₂ ONH	1.466	(2.2)
SF ₂ NCOF	1.474	(2.1)
SF ₂ NCl	1.476	(2.1)
SF ₂ ONCl	1.484	(2.0)
HNSO	1.512	1.9
S ₄ N ₄ F ₄	1.54	1.7
S ₄ N ₃ ⁺	1.55	1.6
ClNSO	1.559	1.5
S ₃ N ₃ Cl ₃	1.605	1.4
S ₄ N ₄	1.63	1.2
S ₄ N ₄ F ₄	1.66	1.1
S ₄ N ₄ H ₄	1.67	1.1
NH ₂ SO ₃ H	1.73	0.8

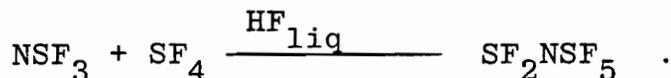
in the gas phase, the nature and complexity of the observed microwave spectrum is such that trace amounts of other rotamers cannot be precluded.

A reasonable, though not unique, structure for N-fluoroformyliminosulfur difluoride was obtained by a least-squares fit of the ground state moments and by assuming reasonable values for some of the bonding parameters. In order to obtain an unambiguous r_0 structure for SF_2NCOF , isotopically enriched samples of $\text{SF}_2\text{N}^{13}\text{COF}$, $\text{SF}_2^{15}\text{NCOF}$, and $\text{SF}_2\text{NC}^{18}\text{OF}$ would have to be prepared and their rotational spectra assigned.

THE LOW RESOLUTION MICROWAVE SPECTRUM AND CONFORMATION
OF PENTAFLUOROSULFANYLIMINOSULFUR DIFLUORIDE

A. Experimental

The sample of pentafluorosulfanyliminosulfur difluoride used in this investigation was prepared by D.E. Maurer and J.S. Thrasher of the Department of Chemistry, Virginia Polytechnic Institute and State University, by the reaction⁶⁵



The product yield was 75-80%⁶⁶ with the major impurities being unreacted SF_4 and NSF_3 , and trace amounts of SOF_2 . Trace impurities of NSF_3 and SOF_2 in the initial sample were identified by their microwave spectra. The microwave spectrum of SF_4 is rather weak and was not observed. The impurities were removed by passing the sample through a -119°C trap (ethyl bromide) and -78°C trap (Dry Ice-ethanol). Following the low temperature distillations, the infrared spectrum, mass spectrum and ^{19}F -NMR spectrum of SF_2NSF_5 were indistinguishable from those given in the literature.^{65,67} Moreover, no impurity lines were detected in the microwave spectrum.

At room temperature pentafluorosulfanyliminosulfur difluoride (B.P. = 43°C), is a clear liquid, with a vapor pressure of 20 cm. Although SF_2NSF_5 is thermally stable,

it does undergo slow hydrolysis to yield the unstable $\text{SF}_5\text{N}=\text{S}=\text{O}$.^{65,67} In light of this care was taken to keep the sample moisture free.

The spectrometer used in this investigation is the same as that described in Chapter III.

The low resolution microwave spectrum of pentafluoro-sulfanyliminosulfur difluoride was recorded from 12.3 - 26.5 GHz at room temperature and at dry ice temperature. A Stark voltage of 1000 volts base-to-peak and high sample pressures, 20-50 μ , were used. Figure XI contains the spectrum from 18.0 to 26.5 GHz. Measurement of the band centers was accomplished in the same manner as described for N-fluoroformyliminosulfur difluoride.

Ten ^aR type bands and five ^cQ type bands were observed and were assigned to the normal isotopic species of SF_2NSF_5 . The assignment is presented in Table XIX.

B. Analysis of Spectrum

Pentafluorosulfanyliminosulfur difluoride may be considered to contain an asymmetric frame NSF_2 linked via a single bond to a symmetric top SF_5 . Viewed in this manner, the possibility of internal rotation of the SF_5 group with respect to the rest of the molecule exists. When the internal rotor is a symmetric top, i.e., has a three-fold axis or higher symmetry, the moments of inertia are inherently

18000

20000

22000

24000

26000

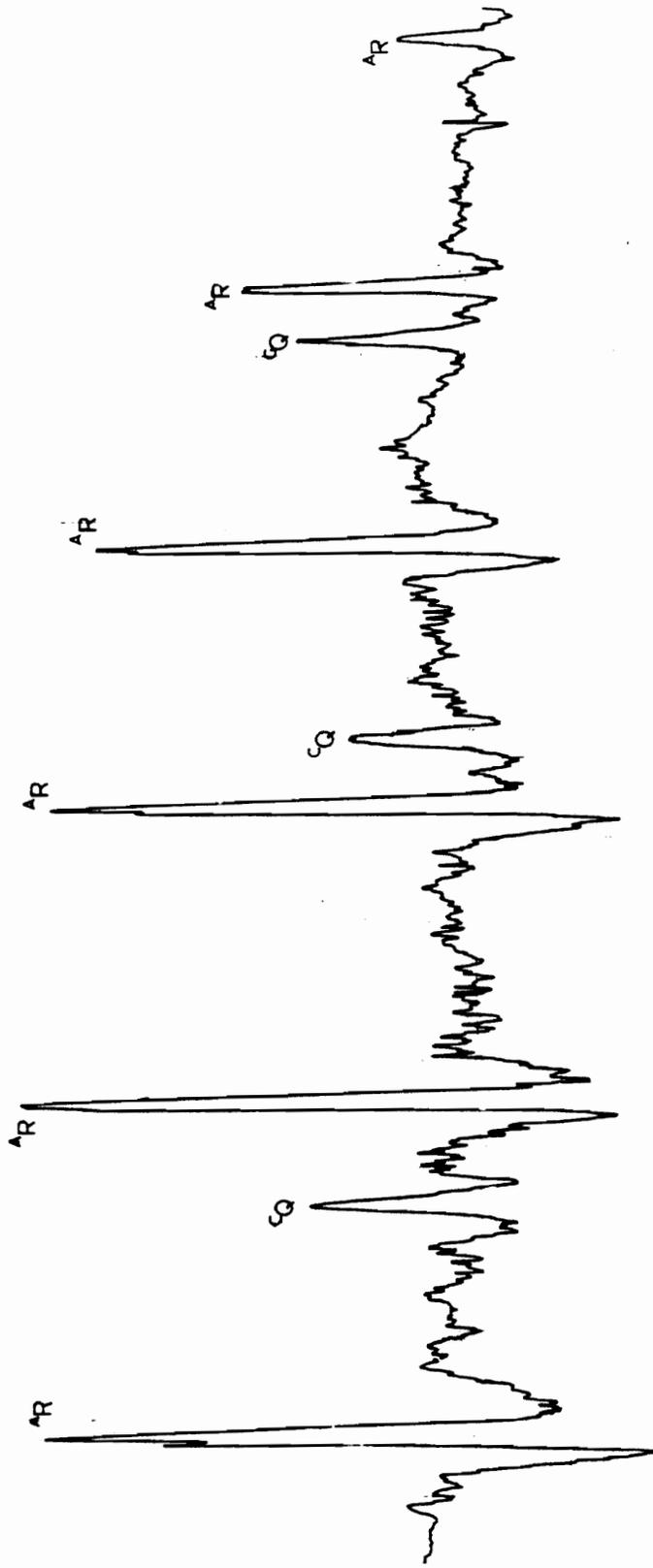


Figure XI. Low Resolution Microwave Spectrum of Pentafluorosulfanyliminosulfur Difluoride

Table XIX
Low Resolution Microwave Spectral Data of
Pentafluorosulfanyliminosulfur Difluoride

^aR-type Bands

J+1	ν (MHz) ^a	B+C(MHz) ^b
8	12305 ± 10	1538 ± 1
9	13845	1538
10	15375	1538
11	16915	1538
12	18470	1539
13	20000	1539
14	21545	1539
15	23090	1539
16	24620	1539
17	26160	1539

Continued

Continuation of Table XIX
 Low Resolution Microwave Spectral Data of
 Pentafluorosulfanyliminosulfur Difluoride
^cQ-type Bands

$K_{-1} + \frac{1}{2}$	ν (MHz) ^a	2A-B-C(MHz) ^b
5.5	13125 ± 15	2386 ± 3
6.5	15520	2388
7.5 ^c
8.5	20310	2390
9.5	22715	2391
10.5	25090	2390

a. Estimated experimental error.

b. Quoted uncertainty limits based on estimated experimental error of ν .

c. This band was not observed due to inadequate emission beyond 17.9 GHz by 12.3 - 18.0 GHz BWO.

invariant to the internal rotation angle.³⁷ Thus, the internal rotation of the SF_5 group in SF_2NSF_5 cannot change the moments of inertia. This occurs because the locus traced by the SF_5 top in the plane perpendicular to its C_4 symmetry axis is a circle. Figure XII contains a model which depicts this internal rotation problem. Since the low resolution microwave spectrum is sensitive only to rotations which depend upon the moments of inertia, this degree of rotational freedom will not be further considered, except to say that it might manifest itself as splittings in the high resolution spectrum.

Equally so, pentafluorosulfanyliminosulfur difluoride may also be viewed as containing two asymmetric tops, SF_2 and NSF_5 , linked by a $N=S$ double bond. Because both groups are asymmetric, changes in the moments of inertia may occur as the SF_2 and NSF_5 units assume different positions relative to the $N=S$ linkage. Some orientations of these two groups may be more favorable than others; SF_2NSF_5 may exist in two or more stable configurations.

The low resolution microwave spectrum of SF_2NSF_5 , which contained only one set of R type bands and one set of Q type bands, is supportive of only one stable configuration. The isomer which gave the observed spectrum can be determined by matching the experimental values of $B+C$ and $2A-B-C$ to those calculated from reasonable models.

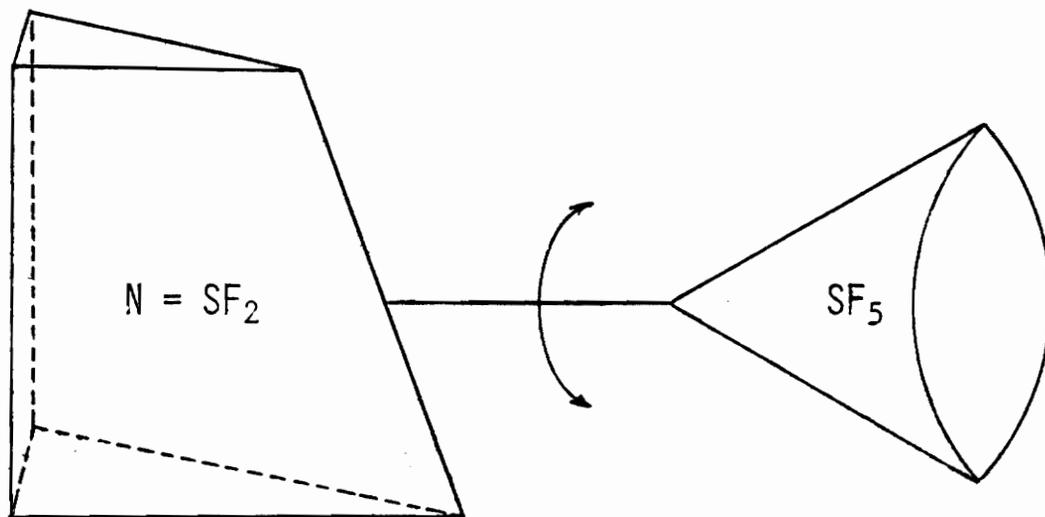


Figure XII. Internal Rotation Problem in Pentafluoro-sulfanylimino Difluoride

For the experimental frequencies of the R-type bands, the equation⁸

$$\nu = (B+C)(J+1)$$

yielded an average value of $B+C = 1538 \pm 1$ MHz. An average value of $2A-B-C = 2389 \pm 2$ MHz was obtained using the equation⁸

$$\nu = (2A-B-C)(K_{-1} + \frac{1}{2})$$

and the observed peak frequencies of the Q band series. From the average value of $B+C$ and the average value of $2A-B-C$, the A rotational constant is determined as 1964 ± 3 MHz.

A tenable structure for pentafluorosulfanyliminosulfur difluoride was derived by compounding the $N=SF_2$ parameters from chloroiminosulfur difluoride,¹⁷ the SF_5 parameters from sulfur hexafluoride,²¹ and the NS single bond distance and the F_aSN angle from difluoroamino sulfur pentafluoride.²⁴ Since no gas-phase value for a SNS angle involving the hybridization scheme $sp^3-sp^2-sp^3d^2$ could be found in the literature, this angle was varied systematically from $110^\circ - 140^\circ$ by 2° increments. Additionally, the heavy atoms S(IV), N, and S(VI) were assumed to lie in a plane which bisects $\angle FSF$ of the $N=SF_2$ group. The approximate structure used in fitting the LRMW spectrum for the

purpose of conformational analysis is presented in Table XX.

Approximate values for the low resolution rotational parameters were calculated for the cis and trans isomers shown in Figure XIII by assuming the gross geometry given in Table XX and by optimizing the angle SNS until agreement between theory and experiment was achieved. The geometry optimization revealed that the LRMW rotational parameters of the trans isomer could not be brought into agreement with those observed for any reasonable set of structural parameters. However, when $\angle \text{SNS} = 132^\circ$ the computed, rotational parameters of the cis isomer were quite compatible with those extracted from the LRMW spectrum. Table XXI contains the calculated and observed low resolution spectral data.

C. Discussion

The low resolution microwave spectrum of pentafluoro-sulfanyliminosulfur difluoride, which contained only one set of R type bands and one set of Q type bands, indicates the existence of only one stable configuration of this molecule in the gas phase. The observed spectrum was identified as due to the cis form of this molecule by means of fitting the observed LRMW rotational parameters B+C and 2A-B-C to those calculated from tenable models.

Table XX
Assumed Structure of
Pentafluorosulfanyliminosulfur Difluoride^a

Structural Parameter	Derived Source	Technique	Ref.
$r(\text{N}=\text{S}) = 1.476$	SF_2NCl	Electron Diffractions	17
$r(\text{S}-\text{F})^{\text{b}} = 1.596$	"	"	"
$\angle \text{NSF} = 111.2$	"	"	"
$\angle \text{FSF}^{\text{b}} = 89.8$	"	"	"
$r(\text{N}-\text{S}) = 1.696$	SF_5NF_2	"	24
$\angle \text{F}_a \text{SN} \approx 180$	"	"	"
$r(\text{S}-\text{F})^{\text{c}} = 1.57^{\text{d}}$	SF_6	"	21
$\angle \text{FSF}^{\text{c}} = 90, 180$	"	"	"
$\angle \text{SNS} = 110-140$	—	—	see text

- a. Bond lengths are in Å, bond angles in degs.
- b. Of $-\text{N}=\text{SF}_2$ gp.
- c. Of $-\text{SF}_5$ gp.
- d. Value reported represents the average of two independent investigations.

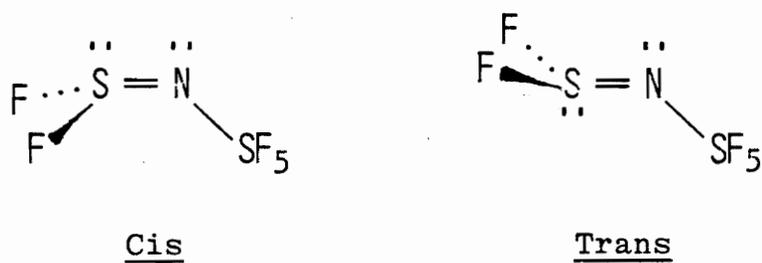


Figure XIII. Cis and Trans Isomers of Pentafluorosulfanyliminosulfur Difluoride

Table XXI
 Comparison of Calculated and Observed
 LRMW Rotational Parameters of
 Pentafluorosulfanyliminosulfur Difluoride

Isomer	B+C(MHz)	2A-B-C(MHz)	A(MHz)	κ
Cis	1549	2435	1992	-0.95
Trans	1284	2932	2113	-0.94
observed ^a	1538 \pm 1	2389 \pm 2	1964 \pm 3	-0.98 ^b

a. Uncertainty limits quoted are the estimated uncertainty in the band maxima divided by the average $J+1$ value or average $K_{-1} + \frac{1}{2}$ value appropriate for the spectrum.²

b. Kappa estimated from linewidth at half-intensity.

Although the calculated rotational parameters of the assumed structure for the cis isomer do not fall within the experimental error of the observed rotational parameters, this does not discredit the assignment of the observed spectrum as belonging to the cis isomer. All assumed structures are inherently somewhat uncertain. Steinmetz⁸ has observed that low resolution rotational constants can usually be calculated using bonding parameters from spectroscopic data of similar molecules with less than a 5% error. In this regard, examination of Table XXI shows that all the experimental rotational parameters fall well within the 5% uncertainty associated with the assumed structure.

Citing the nature of the temperature-dependent fluorine-19 nuclear magnetic resonance spectra of SF_2NSF_5 dissolved in propane, Shanzer²⁵ contends that a second rotameric form involving rotation about the nitrogen-sulfur double bond exists. Since the high resolution spectrum was not assigned, small amounts of the trans isomer, or a relatively nonpolar species cannot be precluded. Due to the large number of fluorines, a complete structure of SF_2NSF_5 cannot be obtained from the assignment of the rotational spectrum.

LITERATURE CITED

1. R. Varma and L. W. Hrubesh, Chemical Analysis by Microwave Rotational Spectroscopy (Wiley, New York, 1979).
2. M. S. Farag and R. K. Bohn, *J. Chem. Phys.* 62, 3946 (1975).
3. W. Gordy and R. L. Cook, Microwave Molecular Spectra (Interscience, New York, 1970).
4. C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill, New York, 1955).
5. S. J. Borchert, *J. Mol. Spectrosc.* 57, 312 (1975).
6. T. M. Sugden and C. N. Kenney, Microwave Spectroscopy of Gases (Van Nostrand Company, London, 1965).
7. N. S. True and R. K. Bohn, *J. Chem. Phys.* 62, 3951 (1975).
8. W. E. Steinmetz, *J. Am. Chem. Soc.* 96, 685 (1974).
9. E. B. Wilson, *Chem. Soc. Rev.*, 293 (1972).
10. V. W. Laurie, *Acc. Chem. Res.* 3, 331 (1970).
11. L. H. Scharpen and V. W. Laurie, *Anal. Chem.* 44, 378R (1972).
12. E. M. Bellott, Jr. and E. B. Wilson, *J. Mol. Spectrosc.* 66, 41 (1977).
13. O. Glemser and R. Mews, *Adv. Inorg. Chem. Radiochem.* 14, 333 (1972).
14. O. Glemser, *Int. J. Sulfur Chem.* 6, 35 (1971).
15. W. H. Kirchhoff and E. B. Wilson, *J. Am. Chem. Soc.* 84, 334 (1962).
16. W. H. Kirchhoff and E. B. Wilson, *J. Am. Chem. Soc.* 85, 1726 (1962).

17. J. Haase, H. Oberhammer, W. Zeil, O. Glemser, and R. Mews, *Z. Naturforsch.* 25A, 153 (1970).
18. R. Kebababcioglu, R. Mews and O. Glemser, *Spectrochim. Acta.* 28A, 1593 (1972).
19. J. E. Griffiths and D. F. Sturman, *Spectrochim. Acta.* 25A, 1355 (1969).
20. R.R. Karl, Jr. and S.H. Bauer, *Inorg. Chem.* 14, 1859 (1975).
21. L. E. Sutton, Tables of Interatomic Distances and Configuration in Molecules and Ions (The Chemical Society, London, 1958).
22. R. Kewley, K. S. R. Murty and T. M. Sugden, *Trans. Faraday Soc.* 56, 1732 (1960).
23. R. A. Crawford, F. B. Dudley and K. Hedberg, *J. Am. Chem. Soc.* 81, 5287 (1959).
24. J. Haase, H. Oberhammer, W. Zeil, O. Glemser and R. Mews, *Z. Naturforsch.* 26A, 1333 (1971).
25. A. Shanzer, Ph.D. thesis, Virginia Polytechnic Institute and State University (1976).
26. A. F. Clifford and C. S. Kabayashi, *Inorg. Chem.* 4, 511 (1965).
27. J. K. Ruff, *Inorg. Chem.* 5, 1787 (1966).
28. H. W. De Wijn, *Rev. Sci. Instr.* 32, 735 (1961).
29. L. Pierce and L. C. Krisher, *J. Chem. Phys.* 31, 875 (1959).
30. C. C. Costain and J. M. Dowling, *J. Chem. Phys.* 32, 158 (1960).
31. O. L. Stiefvater and E. B. Wilson, *J. Chem. Phys.* 50, 5385 (1969).
32. J. J. Keirns and R. F. Carl, Jr., *J. Chem. Phys.* 48, 3773 (1968).
33. G. Williams and N. L. Owens, *Trans. Faraday Soc.* 67, 950 (1971).

34. H. W. Kroto, Molecular Rotation Spectra (Wiley, New York, 1975).
35. D. J. Finnigan, C. W. Gillies, R. D. Suenram, E. B. Wilson and H. Karlsson, *J. Mol. Spectrosc.* 57, 363 (1975).
36. D. G. Lister and N. L. Owen, *J. Chem. Soc. Faraday Trans. II* 69, 1304 (1973).
37. J. E. Wollrab, Rotational Spectra and Molecular Structure (Academic, New York, 1967).
38. M. L. Gum, Ph.D. thesis, Virginia Polytechnic Institute and State University (1974).
39. D. Kivelson and E. B. Wilson, *J. Chem. Phys.* 21, 1229 (1953).
40. J. K. G. Watson, *J. Chem. Phys.* 48, 181 (1968).
41. W. H. Kirchhoff, *J. Mol. Spectrosc.* 41, 333 (1972).
42. C. C. Costain, *J. Chem. Phys.* 29, 864 (1958).
43. J. Kraitchman, *Am. J. Phys.* 21, 17 (1953).
44. P. Cassoux, R. L. Kuczkowski, and R. A. Creswell, *Inorg. Chem.* 16, 2959 (1977).
45. R. H. Schwendeman, "Critical Evaluation of Chemical and Physical Structural Information", National Academy of Sciences, Washington, D.C., 1974.
46. W. H. Kirchhoff, *J. Am. Chem. Soc.* 91, 2437 (1969).
47. V. M. Rao, J. T. Yardley, and R. F. Curl, *J. Chem. Phys.*, 42, 284 (1965).
48. W. Caminati and A. M. Mirri, *J. Mol. Spectrosc.* 66, 368 (1977).
49. H. Oberhammer, *Z. Naturforsch.* 25A, 1497 (1970).
50. U. Biermann and O. Glemser, *Chem. Ber.* 100, 3795 (1967).
51. B. Cohen and A. G. MacDiarmid, *J. Chem. Soc. A*, 1780 (1966).

52. V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.* 63, 37 (1941).
53. W. Gordy, *J. Chem. Phys.* 15, 81 (1947).
54. L. Pauling, *Nature of the Chemical Bond*, 3rd ed. (Cornell Univ. Press, Ithaca, N.Y., 1960).
55. D. R. Lide, *J. Chem. Phys.* 37, 2074 (1962).
56. D. R. Lide and M. Jen, *J. Chem. Phys.* 40, 252 (1964).
57. E. A. Cherniak and C. C. Costain, *J. Chem. Phys.* 45, 104 (1966).
58. P. D. Foster, V. M. Rao, and R. F. Curl, *J. Chem. Phys.* 43, 1064 (1965).
59. O. Oberhammer, O. Glemser, and H. Klüver, *Z. Naturforsch.* 29A, 901 (1974).
60. N. J. D. Lucas and J. G. Smith, *J. Mol. Spectrosc.* 43, 327 (1972).
61. O. Glemser, *Endeavor* 28, 86 (1969).
62. O. Glemser and M. Fild, in *Halogen Chemistry*, ed. V. Gutmann, Vol. 2, pp 1-30 (Academic Press, London and New York, 1967).
63. A. Müller, O. Glemser and B. Krebs, *Z. Naturforsch.* 22B, 550 (1967).
64. O. Glemser, A. Müller, D. Böhler, and B. Krebs, *Z. Anorg. Allgem. Chem.* 357, 185 (1968).
65. A. F. Clifford and J. W. Thompson, *Inorg. Chem.* 5, 1424 (1966).
66. D. E. Maurer, private communication.
67. B. Cohen, T. R. Hooper, and R. D. Peacock, *Chem. Comm.*, 32 (1966).

APPENDIX A

Description of the Computer Programs

1. Moment of Inertia Program

The Moment of Inertia computer program, developed by R.A. Beaudet and W. R. Pauly, calculates the principal moments of inertia of a molecule from the atomic masses, bond length, and bond angles. The bond lengths and bond angles are entered into the program in terms of three arbitrary atoms: atom 1, which defines the origin; atom 2, which determines the +x direction; and atom 3, which defines the +xy-plane. The center of mass is computed and the origin of the coordinate system is moved from atom 1 to the center of mass. This allows the center of mass coordinates of each atom to be computed. Next, a rotational transformation from the center of mass coordinate system to the principal axis system is performed. Computation of the principal axis coordinates of each atom, the principal moments of inertia, and the rotational constants then follows.

2. Rigid Rotor Program

The Rigid Rotor computer program, which was written by R.A. Beaudet, calculates, for any asymmetric rotor, the rotational energy level from $J=1-40$, and the transition

frequencies of the allowed transitions. Computational options include the calculation of the line strengths and the quadrupole and Stark corrections to the energy levels. Depending upon the computational route desired, data to be read into the program might include some or all of the following: rotational constants, dipole selection rules, magnitude of the dipole components, frequency limits, limits on J, and the diagonal elements of the quadrupole tensor.

3. Semirigid Rotor Fit Program

The Semirigid Rotor Fit computer program, which was developed by W.H. Kirchhoff, performs an iterative least-squares fit of the centrifugal distortion constants in the Watson formulation. Watson's Hamiltonian for the P^4 terms may be written as

$$H = A''P_a^2 + B''P_b^2 + C''P_c^2 + \frac{1}{4} \sum_{\alpha=a,b,c} \tau'_\alpha P_\alpha^4 + \tau_1 P_1^4 + \tau_2 P_2^4 + \tau_3 P_3^4$$

where P_1^4 , P_2^4 , and P_3^4 are lengthy functions of A' , B' , C' , P_a^2 , P_b^2 , and P_c^2 . The value of the distortion constant τ_3 is dependent upon the values of the other distortion constants. Thus τ_3 remains indeterminable until completion of the fit, at which time, it is evaluated by the expression

$$\begin{aligned} \tau_3 = & \left(\frac{A'+B'+C'}{B'-A'} \right) \tau'_{aabb} + \left(\frac{A'+B'+C'}{A'-C'} \right) \tau'_{aacc} \\ & + \left(\frac{A'+B'+C'}{C'-B'} \right) \tau'_{bbcc} \end{aligned}$$

In certain cases, to fit the rotational spectrum with residuals of the same magnitude as the measurement error, it may be deemed necessary to incorporate P^6 terms in the semirigid rotor Hamiltonian. Watson's Hamiltonian for the P^6 terms has the form

$$\begin{aligned} H_6 = & H_J P^6 + H_{JK} P^4 P_a^2 + H_{KJ} P_a^4 P^2 + H_K P_a^6 \\ & + h_J (P^4) (P_b^2 - P_c^2) + h_{JK} P^2 [P_a^2 (P_b^2 - P_c^2) + (P_b^2 - P_c^2) P_a^2] \\ & + h_K [P_a^4 (P_b^2 - P_c^2) - (P_b^2 - P_c^2) P_a^4] \end{aligned}$$

With the incorporation of the P^6 terms, the number of centrifugal distortion constants totals fifteen. The number of distortion constants to be fit is governed by the number and type of transitions assigned, as well as the nature of the molecule itself. A rigid rotor fit, by this program, is achieved by fitting low J transitions to only the three rotational constants: $A, B,$ and C .

The necessary input data consist of the approximate rotational constants, the dipole moments, the experimental frequency and assigned quantum numbers of each transition

to be fit, and the number and type of distortion constants to be determined.

4. STRFTQ Program

The computer program STRFTQ, developed by R.H. Schwendeman, adjusts internal coordinates to fit the experimental moments of inertia and assumed constraints in bond angles or bond lengths by an iterative least squares procedure. The least squares logic involves the determination of

$$(F_J - F_J^{\circ}) = \sum_{k=1}^{KX} \left(\frac{\partial F_J^{\circ}}{\partial q_k} \right) (q_k - q_k^{\circ})$$

where

F_J = experimental parameter, e.g., moment of inertia distance or angle

F_J° = calculated parameter determined from the trial set of coordinates q_k°

q_k° = trial set of coordinates

q_k = new set of coordinates determined after each iteration

KX = number of internal coordinates adjusted

J = index specifying the experimental parameter for each experimental parameter F_J fitted.

In this program, the heart of the algorithm is to attain the best set of $\delta q = q_k - q_k^0$ consistent with the experimental parameter F_J . After each iteration, a new set of trial coordinates is computed by the relation $q_k^{\wedge\wedge} = q_k^{\wedge} + \delta_{qk}$. The iteration is deemed complete when all the δq 's or all the δF_J 's are smaller than a pre-set tolerance, or when the number of iterations exceeds a pre-set maximum.

After completion of the iteration process, the program computes the final values of the coordinates, moments of inertia, planar second moments, and rotational constants. Then the final values of the coordinates are used to evaluate the bond lengths and bond angles, as well as the derivatives of these quantities with respect to each internal coordinate. The program also computes the standard deviation of the fit of the moments and the uncertainties of the adjusted internal coordinates. The latter are then propagated into uncertainties in each bond length and bond angle.

Besides the indicators used to control the flow of the program, required input data constitutes a trial set of internal coordinates, atomic masses, experimental rotational constants, and the experimental parameters to be fit. The experimental parameters to be fit include moments of inertia, distances, angles, or sums and differences of these quantities. Since internal coordinates,

rather than Cartesian coordinates, are adjusted, first moments and products of inertia are not among the experimental parameters to be fit.

VITA

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Sharon Rose Bailey

THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF
N-FLUOROFORMYLIMINOSULFUR DIFLUORIDE AND
PENTAFLUOROSULFANYLIMINOSULFUR DIFLUORIDE

by

Sharon Rose Bailey

(ABSTRACT)

The ground state rotational spectrum of N-fluoroformyl-
iminosulfur difluoride has been investigated by low resolu-
tion microwave spectroscopy in the 12.4 - 26.4 GHz region and
by high resolution microwave spectroscopy in the 18.0 - 26.4
GHz region. Five ^aR-type and two ^bQ-type low resolution
bands were assigned to the normal isotopic species. The low
resolution parameters are $B+C = 2913 \pm 2$ MHz and $2A-B-C =$
 6230 ± 20 MHz. In the high resolution spectrum, sixty-five
transitions of the ³²SF₂NCOF species and twelve transitions
of the ³⁴SF₂NCOF species were assigned. A centrifugal dis-
tortion fit of the assigned transitions of the ³²SF₂NCOF
species gave $A = 4563.584 \pm 0.085$ MHz, $B = 1476.855 \pm 0.048$
MHz, $C = 1436.517 \pm 0.043$ MHz, $\tau_1 = -0.0383 \pm 0.0036$ MHz,
 $\tau_2 = -0.008 \pm 0.0012$ MHz, $\tau_3 = -3.15 \pm 0.25$ MHz, $\tau_{bbbb} =$
 0.0036 ± 0.0013 MHz, $\tau_{cccc} = 0.0035 \pm 0.0014$ MHz, $h_J = -0.311$
 $\pm 0.070 \times 10^{-5}$ MHz, and $h_{JK} = 0.132 \pm 0.027 \times 10^{-5}$ MHz.
The rigid rotor fit of the ³⁴SF₂NCOF species gave $A = 4526.27$
 ± 0.99 MHz, $B = 1466.229 \pm 0.040$ MHz, $C = 1423.795 \pm 0.035$ MHz.

Spectral evidence for only one predominant isomer of

N-fluoroformyliminosulfur difluoride was observed in the gas phase. The conformation about the NS double bond was determined to be cis and the fluorine of the carbonyl fluoride group was found to eclipse the lone pair of electrons on nitrogen. Due to a lack of extensive isotopic substitution, several of the bonding parameters had to be assumed. The assumed parameters were $r_{\text{CO}} = 1.181 \text{ \AA}$, $r_{\text{CF}} = 1.348 \text{ \AA}$, $\angle\text{OCF} = 121.35^\circ$, and $\angle\text{NCO} = 123.80^\circ$. From a least squares fit of the moments of inertia of the $^{32}\text{SF}_2\text{NCOF}$ and $^{34}\text{SF}_2\text{NCOF}$ species, the remaining structural parameters were determined to be $r_{\text{NS}} = 1.474 \pm 0.005 \text{ \AA}$, $r_{\text{CN}} = 1.448 \pm 0.005 \text{ \AA}$, $r_{\text{SF}} = 1.606 \pm 0.002 \text{ \AA}$, $\angle\text{SNC} = 124 \pm 1^\circ$, $\angle\text{NSF} = 108.6 \pm 0.3^\circ$, and $\angle\text{FSF} = 91.7 \pm 0.2^\circ$.

The low resolution microwave spectrum of pentafluoro-sulfanyliminosulfur difluoride consisted of an intense series of ^aR -type bands and a weak set of ^cQ -type bands. Ten ^aR -type bands and five ^cQ -type bands were observed in the region from 12.3 to 26.4 GHz and were assigned to one isomeric form of the normal isotopic species. The low resolution parameters were determined to be $B+C = 1538 \pm 1 \text{ MHz}$, and $2A-B-C = 2389 \pm 2 \text{ MHz}$. Evidence for only one conformer of this molecule was observed in the gas phase. By assuming reasonable models, the rotamer which is most consistent with the observed spectral data has a cis conformation about the NS double bond.