Inorg. Chem. **1982**, *21*, 1607-1616 **1607**

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Novel Sulfur–Nitrogen–Fluorine Compounds. Synthesis and Properties of SF_5NClF, SF_5NHF, and $FN{=}SF_4$ and the Molecular Structure and Vibrational Analysis of $FN{=}SF_4$

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Received June 29, 1981

Pentafluoro(fluorochloroamido)sulfur, SF_5NFCl, can be synthesized from NSF_3 by low-temperature reaction with ClF, followed by reaction with fluorine. Reduction of SF_5NClF with mercury in trifluoroacetic acid forms (fluoroimido)-pentafluorosulfur, SF_5NHF, in high yield. Dehydrofluorination of SF_5NFH with KF results in (fluoroimido)tetrafluorosulfur, $FN{=}SF_4$. The imine is an unusual pentacoordinate molecule which does not undergo positional exchange of the sulfur fluorines according to ^{19}F NMR. A complete vibrational analysis of $FN{=}SF_4$ based on C_s symmetry has been carried out and found to be in good agreement with the related molecules OSF_4, $CH_2{=}SF_4$, and SF_4. The gas-phase structure was determined by joint analysis of electron diffraction and microwave spectroscopic data. The structure contains a relatively long S=N bond, short N—F bond, and a large difference in the nonequivalent axial S—F bonds.

Introduction

A large number of interesting sulfur–nitrogen–fluorine compounds have been characterized in which sulfur is commonly in the II, IV, or VI oxidation state.[1,2] In many cases, sulfur(VI) compounds resemble related fluorocarbon analogues. Thus CF_3NF_2, CF_3NCl_2, and CF_3NH_2 correspond to SF_5NF_2, SF_5NCl_2, and SF_5NH_2. Unsaturated compounds of sulfur also have many fluorocarbon analogues. Thus $FC{\equiv}N$ and $CF_2{=}NCl$ are related to $FS{\equiv}N$ and $SF_2{=}NCl$.

Recently, methods for the synthesis of RCF_2NClF, RCF_2NHF, and $RCF{=}NF$ (R = Cl or perfluoroalkyl) were found starting with $RC{\equiv}N$.[3,4]

$$RCN \xrightarrow{ClF/F_2} RCF_2NClF \xrightarrow{Hg} RCF{=}NF$$
$$\xrightarrow{Hg/CF_3CO_2H} RCF_2NHF$$

Extension of these reactions to the sulfur–nitrogen triple bond in NSF_3 was undertaken to synthesize the unknown analogues SF_5NClF, SF_5NHF, and $FN{=}SF_4$.[5,6] In this paper the synthesis and properties of these new compounds are given in detail. In addition, the novelty of $FN{=}SF_4$ as an unusual pentacoordinate molecule and the simplest perfluorinated sulfur(VI) imine warranted a detailed structural analysis. The gas-phase structure of $FN{=}SF_4$, determined by combined microwave and electron diffraction, is reported along with a complete vibrational analysis of $FN{=}SF_4$ based on C_s symmetry.

Experimental Section

General Data. Volatile compounds were manipulated in a stainless-steel or glass-vacuum system fitted with Teflon-packed stainless-steel valves or glass–Teflon valves, respectively. Connections to the vacuum system were by means of standard taper joints lubricated with Halocarbon grease or by metal compression fittings. Pressures were measured with a precision Bourdon tube manometer. Temperatures were measured with a digital-indicating resistance thermometer. Amounts of materials were measured by direct weighing or by *PVT* measurements, with the assumption of ideal gas behavior.

Molelcular weights were determined by gas density measurements. Vapor pressures were determined at various temperatures with a static method. Data were analyzed by a least-squares fit to both linear and quadratic equations, and the best fit is reported.

Routine IR spectra were recorded on a Perkin-Elmer 457 spectrometer using a 10-cm glass cell fitted with KCl windows. High-resolution spectra were taken on a Perkin-Elmer 180 spectrometer using CsBr or polyethylene windows. Raman spectra were recorded with Spex 1403 double monochromater with an ELSCINT photon-counting detection system. Excitation was by the 632.8-nm line of He-Ne laser (OIP Gent) or the 514.5-nm line of an argon ion laser (Coherent Rad. Lab.). Liquid samples were sealed in 5-mm Pyrex tubes kept at −40 to −50 °C by use of a CTI cryocooler. The usual 90° scattering geometry was employed. Depolarization ratios were determined by turning the polarization of the laser beam with the aid of a half-wave plate and analyzing the scattered light with a sheet polarizer.

Table I. Rotational Constants for $FN{=}SF_4$ in GHz

	A	*B*	*C*
B^i_0	3.457 779 (4)	2.141 710 (4)	1.848 713 (4)
B^i_z	3.455 63 (22)	2.141 00 (7)	1.847 76 (10)
B^i_z(calcd)	3.455 75	2.141 04	1.847 84

NMR spectra were recorded on a JEOL C-6-HL spectrometer. Chemical shifts are reported relative to internal $CFCl_3$ for fluorine and external Me_4Si for protons. Positive shifts are to low field of the reference. Computer analysis of spectra were made with LACOON 3. Mass spectra were taken on a Varian CH7 instrument at 70 eV.

Electron Diffraction. The electron diffraction intensities were recorded with the Balzers diffractograph KDG2[7] at two camera distances (50 and 25 cm) with an accelerating voltage of about 60 kV. The nozzle temperature was about 10 °C; the sample was kept at −73 °C. The camera pressure never exceeded 1.5×10^{-5} torr. The electron wavelength was determined from ZnO diffraction patterns, and the range of scattering angles covered in the experiment was $1.4 \le s \le 17$ Å^{-1} and $8 \le s \le 35$ Å^{-1} for the two camera distances. Two plates for each distance were selected, and intensity data were reduced in the usual way.[8] The averaged molecular intensities in steps of $\Delta s = 0.2$ Å^{-1} are presented in Figure 1 and the radial distribution function in Figure 2.

Microwave Spectrum. The microwave spectra were measured with a conventional Stark spectrometer[9] in the range 8–43 GHz. The Stark field was 400 V cm^{-1} and its frequency 100 kHz. For the vibrational

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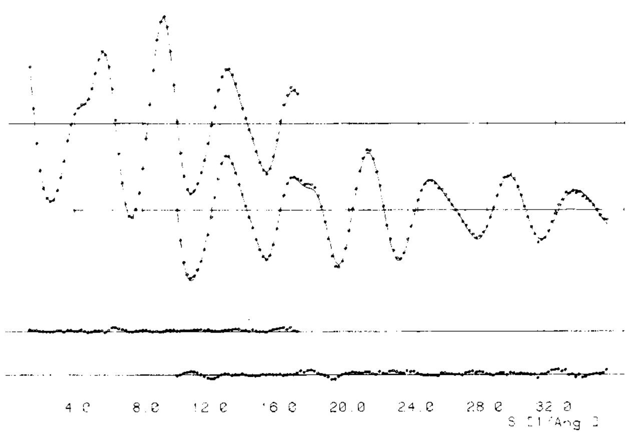

Figure 1. Experimental (O) and calculated (—) molecular intensities and differences for $FN{=}SF_4$.

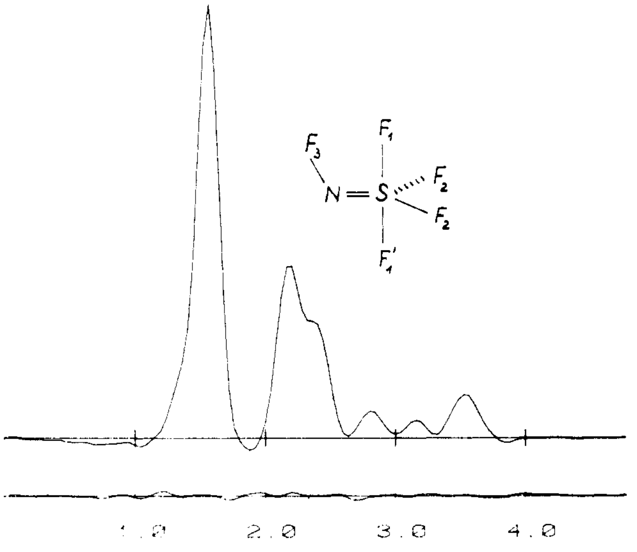

Figure 2. Experimental radial distribution function and difference curve for $FN{=}SF_4$.

ground state, 107 transitions for $J = 2$ to $J = 54$ and up to $K = 17$ were assigned. The B^i_0 rotational constants ($B^i = A, B, C$) are listed in Table I.[10] Error limits are standard deviations of the least-squares fit.

Normal-Coordinate Analysis. All calculations were performed on the IBM 370-163 computer at University Computer Center at Heidelberg. Construction of the **G** matrix was performed via the **B** matrices with standard matrix methods.[11] Redundancies were removed by solving the **B** matrix for zero coordinates and successive orthonormalization of the **U** matrix.[12] A symmetry force field was then calculated by the eigenvector method[13] with a modified version[14] of the Chacon–Matzke[15] program. Refinement of the GVFF constants was made with Schachtschneider's program FPERT.[16]

Reagents. Fluorine, chlorine, CF_3CO_2H, KF, NaF, P_4O_{10}, SF_4, Hg, SbF_5, AsF_5, HCl, $CFCl_3$, $SiCl_4$, and AgNCO and Ag_2SO_4 were obtained from commercial sources and were appropriately purified, if needed, before use. Chlorine monofluoride was prepared by heating equimolar amounts of Cl_2 and F_2 in a Monel bomb at 250 °C for 18 h. Trifluoroacetic acid was prepared by heating excess P_4O_{10} with CF_3CO_2H. Silver difluoride was prepared by burning Ag_2SO_4 in a stream of fluorine gas, followed by pulverization and continued fluorination at ~400 °C. The reagents $Si(NCO)_4$,[17] $SF_2{=}NC(O)F$,[18] and NSF_3[19] were prepared by literature methods.

Preparation of SF_5NClF. Into a 250-mL stainless-steel reactor at −196 °C was condensed 10.0 mmol of $SF_3{\equiv}N$. Chlorine monofluoride (20.0) was then carefully condensed onto the upper walls of the reactor (rapid addition of ClF results in a spontaneous reaction even at −196 °C). The reactor was then placed in a CF_2Cl_2 slush bath at ~−160 °C that contained solid CO_2 and was allowed to warm to −78 °C over 14 h. The reactor was then cooled to −196 °C, and 5.0 mmol of F_2 was added and the reactor warmed again from −160 to −78 °C over 14 h. A second addition of F_2 (5.0 mmol) was then made and the reactor warmed once more from −160 to −78 °C over 11 h.

The contents of the reactor were then pumped through traps at −78, −115, and −196 °C. Some noncondensable gases (F_2 and N_2) were observed. The −196 °C trap contained large amounts of ClF and smaller amounts of SF_6 and other products. The −155 °C trap contained a pale yellow liquid that was pumped through a second −115 °C trap, yielding 7.5 mmol of nearly colorless pure SF_5NClF. The −78 °C trap contained a white solid which was shown by NMR to be $(SF_4NCl)_2$ (~0.5 mmol).

$F^ASF_4{}^BNF^XCl$: bp 24.6 °C; mp glass below −130 °C; mol wt found 196.1; mol wt calcd 195.51; log P (torr) = 7.63970 − 1417.0/T; ΔH_{vap} = 6.48 kcal/mol; ΔS_{vap} = 21.8 eu; IR 932 (sh), 913 (vs), 874 (vs), 775 (m), 701 (w), 597 (m), 547 (vw) 460 (vw) cm^{-1}; NMR ϕ_A* 56.6, ϕ_B* 46.7, ϕ_X* 54.3, br, J_{AB} = 144, J_{AX} = 2.9, J_{BX} = 10.8 Hz.

Preparation of SF_5NHF. Into a 100-mL glass reactor fitted with a glass–Teflon valve were added 20 g of Hg and 6 g of trifluoroacetic acid (TFA). This reactor was then cooled to −196 °C and 8.9 mmol of SF_5NClF was added by vacuum transfer. This mixture was then cooled at 0 °C and stirred for 5 h. The products were then separated by passing through traps at −78, −110, and −196 °C. The −78 °C trap contained TFA. The −110 °C trap contained SF_5NHF and small amounts of TFA, an unknown carbonyl compound and an unknown isocyanate. This mixture was further purified by repeated passes through a −95 °C trap until nearly all the contents of the −110 °C trap had passed through the −95 °C trap. This gave essentially pure SF_5NHF (8.0 mmol) corresponding to a 90% yield. The −196 °C trap contained small amounts of SF_6, $CF_3C(O)F$, and an unknown isocyanate. A small amount of N_2 passed through the −196 °C trap.

$F^ASF_4{}^BNF^XH^M$: bp 24.5 °C; mp −78 °C; mol wt found 163.6; mol wt calcd 161.07; log P (torr) = 7.67283 − 1426.41/T; ΔH_{vap} = 6.53 kcal/mol; ΔS_{vap} = 21.9 eu; IR 3300 (s), 1420 Q (vs), 1084 (s), 993 (s), 942 (m), 902 Q (vs), 871 (vs), 755 (w), 701 (m), 612 Q (s), 566 (s), 458 (w), 367 (vw), 290 (vw) cm^{-1}; NMR ϕ_A* 64.6, ϕ_B* 52.6, ϕ_X* −74.7 (br d), δ_M 8.85 (d quint), J_{AB} = 155, J_{BX} = 14.3, J_{BM} = 4.3, J_{XM} = 45.3 Hz.

Preparation of $FN{=}SF_4$. Potassium fluoride (12 g) was placed in a 250-mL stainless-steel reactor and held under dynamic vacuum for several hours at ~80 °C. The vessel was then cooled to −196 °C, and 3.1 mmol of SF_5NHF was added by vacuum transfer. The reactor was then held at 0 °C for 7 h. The contents were then separated by pumping through traps at −110, −125, and −196 °C. The −110 °C trap contained small amounts of unreacted SF_5NHF and an unidentified carbonyl compound from an impurity in the SF_5NHF. The −196 °C trap contained some SF_6, OSF_2, $CF_3C(O)F$, other unidentified products, and a small ammount of $FN{=}SF_4$. Some N_2 also passed through the −196 °C trap. The −125 °C trap contained $FN{=}SF_4$ (2.6 mmol, 85%) contaminated with small amounts of $CF_3C(O)F$ and OSF_2.

$F_2{}^AF^BF^CS{=}NF^D$: bp −13.3 °C; mp −99 °C; mol wt found 142.7; mol wt calcd 141.07; log P (torr) = 6.87778 − 847.945/T − 49562.3/2; ΔH_{vap} = 5.62 kcal/mol; ΔS_{vap} = 21.7 eu; mass spec (70 eV) m/e 141 (M^+); IR (see Results and Discussion); NMR ϕ_A* 52.7, ϕ_B* 45.0, ϕ_C* 13.2, ϕ_D* −43.9 (A_2BCD spin system),[20] J_{AB} = 213.9, J_{AC} = 194.0, J_{AD} = 19.6, J_{BC} = 10.7, J_{BD} = −92.7, J_{CD} = 226.8 Hz.

Results and Discussion

SF_5NClF. The addition of ClF to NSF_3 was first reported in 1965.[21] Reaction at −78 °C gave low yields of SF_5NCl_2,

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(10) The analysis of the microwave spectra will be published in detail elsewhere.

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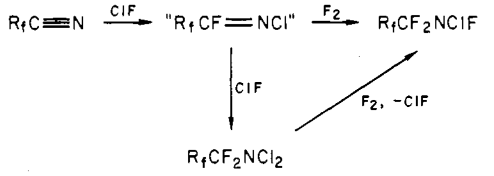
(20) For a picture of the ^{19}F NMR spectrum of $FN{=}SF_4$, see ref 5.

a shock-sensitive yellow liquid stable to ~80 °C. More recently, the reaction of excess NSF_3 with ClF has also been shown to form low yields of $(SF_4NCl)_2$, containing a four-membered $(S-N)_2$ ring system.[1] The reaction of NSF_3 with F_2 does not give the analogous SF_5NF_2 or $(SF_4NF)_2$ compounds, but rather $SF_5N{=}SF_4$.[1]

$$\begin{tikzcd}SF_5N{=}SF_4 & NSF_3 \arrow[l, "F_2"'] \arrow[r, "ClF"] & \text{“}SF_4{=}NCl\text{”} \arrow[r, "ClF"] \arrow[dr] & SF_5NCl_2 \\ & & & (SF_4NCl)_2\end{tikzcd}$$

In the above reactions, considerable SF_6 and N_2 are also formed, along with other products depending on the reaction conditions.

Our interest in NSF_3 was to prepare SF_5NClF by a method similar to that used to prepare R_fCF_2NClF.[3] For the latter, high yields of these materials can be obtained by reaction of R_fCN with a 1:1 mixture of ClF and fluorine. It is reasonably well established that the reaction sequence in this case is



The major path involves the intermediate formation of $R_fCF_2NCl_2$. The reaction of NSF_3 with a 1:1 mixture of ClF/F_2 does not proceed in the same manner. Under a variety of conditions, only 10–20% yields of SF_5NClF were obtained along with many other products including large amounts of SF_6 and N_2. The amount of N_2 formed was very much a function of the initial fluorine concentration, suggesting that fluorine was competing with ClF for the initial reaction with NSF_3. Subsequently, it was found that reaction of NSF_3 with ClF followed by reaction of SF_5NCl_2 with F_2 gave excellent yields of the desired product. However, F_2 attacks the S–N bond in SF_5NCl_2 and addition of the F_2 in 2 alliquots gave higher yields.

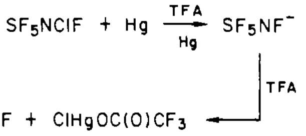
$$NSF_3 + 2ClF \xrightarrow{-160 \text{ to } -78\ ^\circ C} SF_5NCl_2$$

$$SF_5NCl_2 \xrightarrow[-160 \text{ to } -78\ ^\circ C]{0.5F_2} \xrightarrow[-160 \text{ to } -78\ ^\circ C]{0.5F_2} SF_5NClF\ (75\%) + ClF$$

Pentafluoro(fluorochloroamido)sulfur is a stable, nearly colorless liquid at 22 °C. It showed no tendency to undergo spontaneous decomposition during routine handling in the vacuum system. The characterization of the compound by NMR and IR spectroscopy and molecular weight determination is straightforward. The IR spectrum contains three characteristic absorbtions of the SF_5 group at 913, 874, and 597 cm^{-1}.[22] The shoulder at 932 cm^{-1} is reasonable for ν(NF) by comparison with SF_5NF_2[23], HNF_2,[24] and $ClNF_2$.[25] The SO stretching in SF_5O derivatives is above 900 cm^{-1}, and ν(S–N) should considerably lower.[22] The medium band at 775 cm^{-1} may be due to this vibration. The weak band at 701 cm^{-1} is reasonable for ν(NCl) but it might also be due to the SF_5 group.

The NMR spectrum of SF_5NClF exhibits the expected AB_4 second-order spectrum for the SF_5 group with J_{AB} = 144 Hz. The chemical shift of the N–F fluorine is at much lower field than the same fluorine in R_fCF_2NClF.[4]

SF_5NHF. In the case of R_fCF_2NClF derivatives, a positive chlorine can be substituted by a proton from TFA by reaction with mercury.[4] This reaction appears to be quite general and proceeds in high yield with SF_5NClF. The reaction path probably involves the formation of an intermediate SF_5NF^- ion.



Good evidence for perfluoroalkanamine ions has been found with the fluorocarbon system and SF_5NF^- allso appears to be generated by reaction of $FN{=}SF_4$ with active KF. The mercury in this reaction is partially converted to a fine white powder which is believed to be $ClHgOC(O)CF_3$, as shown. Positive identification was not made but the compound is definitely not $HgCl_2$.

(Fluoroamido)pentafluorosulfur is a stable colorless liquid at 22 °C. It shows no tendency toward spontaneous elimination of HF, and no SiF_4 is observed when it is handled in glass. The proton is somewhat acidic as shown by the ^1H NMR at δ 8.85. The ^{19}F NMR gives the expected second-order AB_4 system for the SF_5 group with J_{AB} = 155 Hz. As in the case of R_fCF_2NHF, the fluorine on nitrogen exhibits a large high-field shift (128 ppm) compared to SF_5NClF and a considerably narrower line width. The large $^2J_{FH}$ value of 45.3 Hz is comparable to other *N*-fluoroamines.[4] The IR contains the expected ν(NH) at 3300 cm^{-1} and δ(NH) at 1420 cm^{-1} and the four bands at 902, 871, 701, and 612 are due to the SF_5 group. The remaining bands are reasonable for SF_5NHF but not readily assignable.

$FN{=}SF_4$. For the synthesis of $R_fCF{=}NF$ from R_fCF_2NClF, reaction with mercury at 22 °C was effective in evry case except CF_3NClF. This compound slowly reacts with Hg to give a stable mercurial. Similar behavior might be expected for SF_5NClF, and this was indeed the case. Reaction with Hg under various conditions resulted in absorption of most of the comound by the mercury with only minor amounts of volatile products formed. These were mainly NSF_3, SF_4, SF_6, and N_2. Various solvents were ineffective in producing any $FN{=}SF_4$. The 1,3-dehydrofluorination of SF_5NHF was then the only alternative route available to $FN{=}SF_4$.

The dehydrofluorination of SF_5NHF was first attempted with NaF. At temperatures up to 65 °C, essentially no reaction was observed. A stronger base was clearly needed and KF proved effective. Reaction at 0 °C gave good yields of the desired compound.

$$SF_4NHF + KF \xrightarrow{0\ ^\circ C} FN{=}SF_4 + KF{\cdot}HF$$

In order for this reaction to work effectively, it was necessary for the KF not to be too active. Potassium fluoride which had been fused and finely powdered resulted in low yields and the formation of other products.

(Fluoroimido)tetrafluorosulfur is a monomeric, stable, colorless gas at 22 °C. In contrast to SF_4NCl,[1] it shows no tendency to form a cyclic dimer. It has a remarkably foul smell, and it may be rather toxic. Very minor exposure to the

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(26) (a) In one case, a large amount of heavy material was observed. The molecular weight was very close to $(SF_5N)_2$ and the mass spectrum showed a large SF_5N^+ ion. At the time it was assumed that a 1,1-dehydrofluorination of SF_5NHF had occurred, forming $SF_5N{=}NSF_5$. However, in light of work with $CF_2{=}NF$, which is readily dimerized by KF,[26b] it seems more reasonable that a dimer of $SF_4{=}NF$, SF_5NF-$SF_3{=}NF$, was also formed. The NMR of an impure sample showed the presence of an SF_5 group as well as other sulfur fluorines. This aspect of the chemistry of $FN{=}SF_4$ is currently under investigation. (b) Chang, S.-C.; DesMarteau, D. D. *Polyhedron*, in press.

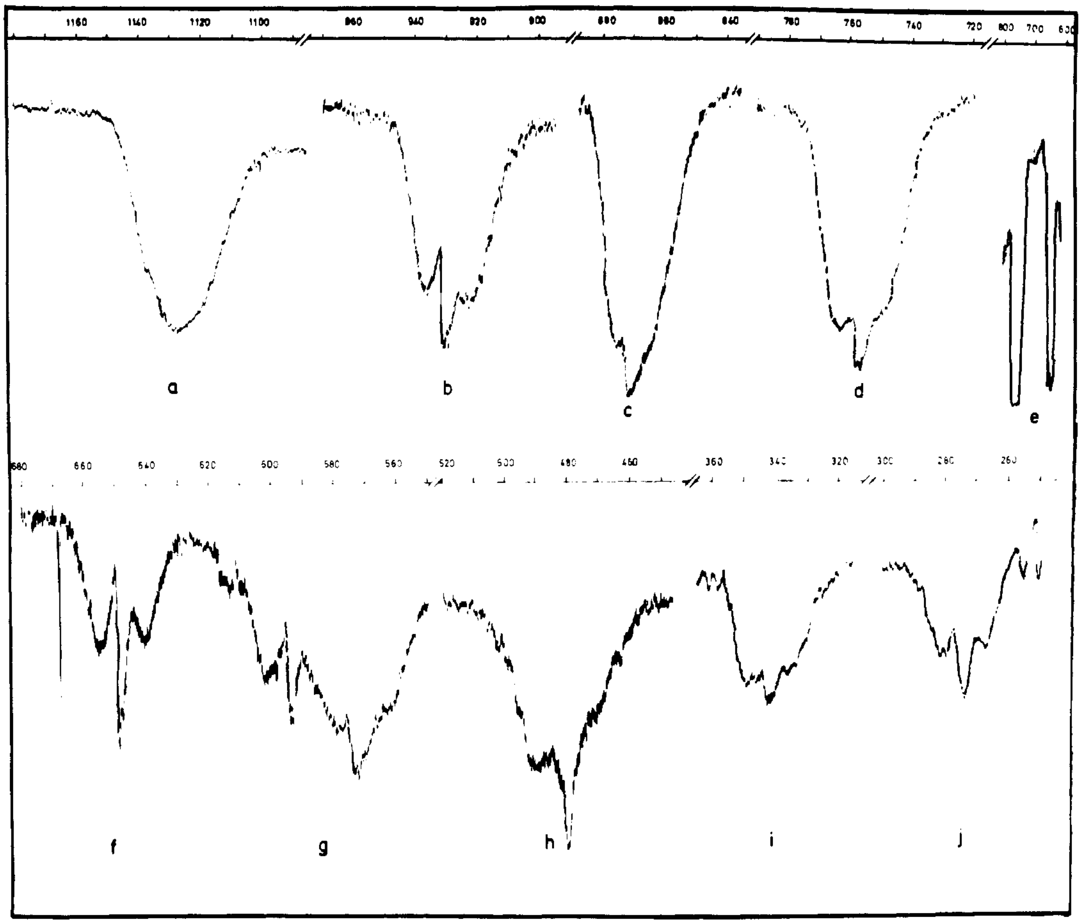

Figure 3. Infrared spectra of $FN{=}SF_4(g)$ at 0.4-cm^{-1} slit and 10 torr [a, c, d, f(2×), g(2×)], 1 torr (b), and 1.0 cm^{-1} slit and 35 torr (h) and 100 torr (i, j).

gas produces rapid nausea. The basic structure of $SF_4{=}NF$ is clearly evident from the ^{19}F NMR. The NMR is explicable on the basis of a rigid trigonal bipyramid in which the SNF plane is aligned with one of the axial fluorines. The rather textbooklike spectrum could be completely analyzed on the basis of A_2BCD spin system.[20] Remarkably, the spectrum does not collapse up to 100 °C, but the lines do broaden somewhat as a function of temperature. This is probably due to quadrupolar effects of ^{14}N. Other examples of related materials do not exhibit the same apparent lack of fluxional behavior. Both $SF_4{=}NCH_3$[1,27] and $SF_4{=}NCF_3$[28] show equivalence of sulfur fluorines at 22 °C and low temperatures are required to observe the nonequivalence of the sulfur fluorines by ^{19}F NMR. Similarly, the related oxide $SF_4{=}O$ is fluxional down to −148 °C, the lowest temperature so far examined.[29] The apparent lack of fluxionality in $FN{=}SF_4$ is similar to $CH_2{=}SF_4$.[30] It is remarkable that such apparently similar compounds show such varying behavior under the scrutiny of ^{19}F NMR.

The acid–base properties of $FN{=}SF_4$ were briefly investigated by reaction with AsF_5 and SbF_5. Reaction of $FN{-}SF_4$ with AsF_5 yields a white solid on warming from −78 °C, which is completely dissociated to $FN{=}SF_4$ and AsF_5 on standing at 22 °C. This appears to be a simple nitrogen-bonded adduct, $FN{=}SF_4{\rightarrow}AsF_5$, and the expected SF_3NF^+ cation is not observed.[31] In contrast, reaction of SbF_5 with $SF_4{=}NF$ results in a violent explosion at ∼−10 °C.[32] Several cationic species related to "SF_3NF^+" are known including SF_3O^+-

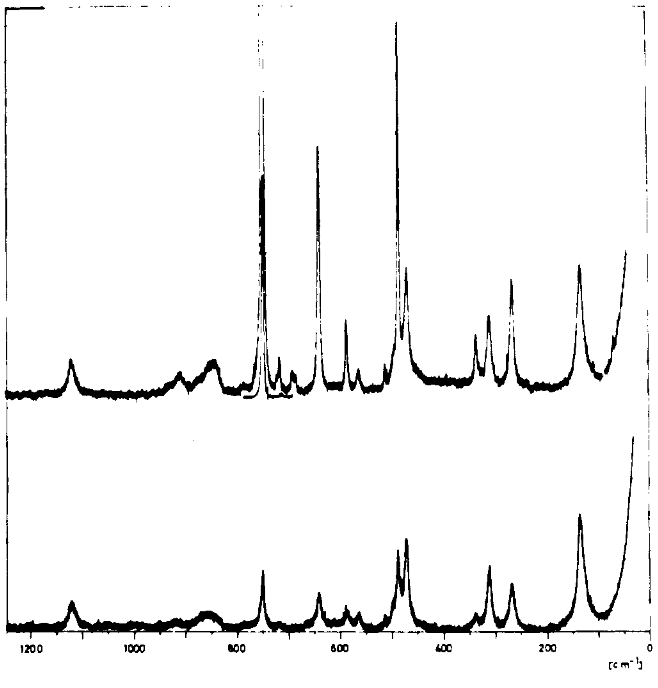

Figure 4. Raman spectrum of $FN{=}SF_4(l)$ at −40 to −50 °C (upper, ‖; lower, ⊥).

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(31) A similar adduct is observed with NSF_3 and AsF_5 or SbF_5: see ref 1, p 888.

Table II. Calculated and Observed Frequency Difference between P- and R-Branch Maxima

band character	PR calcd, cm^{-1}	PR obsd,[a] cm^{-1}	band character	PR calcd, cm^{-1}	PR obsd,[a] cm^{-1}
A	14.1	14.5	C	21.2	20.7
B	10.5	10.1			

[a] Mean values of clearly resolved IR band contours.

AsF$_6^-$[33] and SF$_3$NCH$_3^+$AsF$_6^-$.[27] On this basis, the adduct with AsF$_5$ might well be SF$_5$NF$^+$AsF$_6^-$. However, if this were true, the SbF$_6^-$ adduct would be expected to form readily and to have higher thermal stability.

Vibrational Spectra of FN═SF$_4$. The IR spectra of gaseous FN═SF$_4$ at room temperature and varying pressures are shown in Figure 3. A total of 30 bands were observed in a survey spectrum (not shown in the figure) of a sample at 75-torr pressure. Many of them display a clear PQR structure which can be used as an aid for their assignment. The Raman spectra of liquid samples under $z(yy)x$ and $z(xy)x$ scattering geometry are shown in Figure 4. Fluoroimidotetrafluorosulfur like CH$_2$═SF$_4$[34,35] is closely related to OSF$_4$,[29,36,37] and therefore a general similarity of the vibrational spectra is observed. Introduction of the FN═ group in place of O═ or CH$_2$═ lowers the molecular symmetry from C_{2v} to C_s. Selection rules for the point group C_s predict IR and Raman activity for all of the vibrational modes, but one might regard the influence of the FN═ group as a perturbation only on the C_{2v} symmetry of the SF$_4$ group, and thus one expects low IR intensity for those modes which would transform as A$_2$ in C_{2v}.

For the calculation of the rotational subband structure of the IR spectra, the molecular geometry from electron diffraction was used. This is discussed in the final section of this paper. The principal moments of inertia of FN═SF$_4$ are

$$I_A = 146.2 \text{ amu Å}^2;\|Z \qquad I_B = 236.0 \text{ amu Å}^2;\|X$$
$$I_C = 273.4 \text{ amu Å}^2;\|Y$$

The corresponding rotational constants are $A = 0.115$ cm^{-1}, B 0.072 cm^{-1}, and $C = 0.062$ cm^{-1}. Following the formalism of Seth-Paul,[38] the parameters defining the properties of the prolate asymmetric top are

$$\kappa = \frac{2B - A - C}{A - C} = -0.623 \qquad \rho^* = (A - C)/B = 0.736$$
$$\beta + 1 = A/B = 1.597$$

The separation of P- and R-branch maxima ΔPR is then computed for the different bands and collected in Table II. The agreement between calculated and observed PR splittings is clearly very good. Observed ΔPR can therefore be taken to estimate the direction of the vibrating dipole moment and used as an aid for assignment.

Our assignment of the vibrational spectrum of FN═SF$_4$ is based mainly on arguments of characteristic frequency ranges, on depolarization ratios of the Raman spectra, on qualitative intensity considerations, and on the band contours of IR gas spectra. The highest frequency for a fundamental of FN═SF$_4$ should be the N═S stretch (1000–1200 cm^{-1}). The strong IR, medium-intensity Raman band at 1126 cm^{-1} is asigned to the N═S stretch, ν_1. The strong IR absorption at 870 cm^{-1}, which appears only as a shoulder in the Raman, is assigned to the antisymmetric SF$_1$ (axial) stretch, ν_2. Its mutual intensity distribution in the IR and Raman as well as the B$_\perp$ band contour strongly support this assignment. ν_3, the NF stretch, is not observed in the IR spectra but is observed as a medium-intensity, polarized band at 850 cm^{-1} in the Raman spectra. Its absence in the IR is in agreement with an earlier study,[39] which should have a similar charge distribution on the NF bond. The strongest and highly polarized Raman band, ν_4, at 754 cm^{-1} (IR gas, 757 cm^{-1}) was initially assigned to the symmetric stretch of all four SF bonds in phase, the "breathing mode" of the SF$_4$ group, but the normal-coordinate treatment reveals that the character of this vibration is predminantly equatorial stretching.

A weak band around 700 cm^{-1} (Raman, 697 cm^{-1}) is assigned to the out of phase SF$_1$ (axial stretch with small contributions of equatorial stretch. The out of phase movement of two symmetric stretch modes would explain both the low IR and Raman intensities. Normal-coordinate displacement vectors $\mathbf{L}^{-1}\cdot\mathbf{B}\cdot\mathbf{m}^{-1/2}$[11] applied on the nuclear charges[35] justify the assignment. There is only one stretch frequency in the A″ representation, ν_{11}, the antisymmetric SF$_2$ (equatorial) stretch which is, in analogy to other SF compounds, assigned to the very strong IR band at 929 cm^{-1}.

The bending modes are much more difficult to assign, though the band contours and depolarization ratios facilitate a distinction between A′ and A″ modes. The A″ modes are selected by their depolarization ratio of 0.75 and arranged as follows: ν_{13} 479 cm^{-1}, SF$_4$ rocking; ν_{14} 316 cm^{-1}, SF$_4$ skeletal twist of axial plane against equatorial plane (no intensity in the IR because it arises from an A$_2$ mode of the C_{2v} local symmetry of ═SF$_4$); ν_{15}, 140 cm^{-1}, FN torsion around SN bond with no IR intensity expected from inspection of the charge movement. The strong IR absorption at 594 cm^{-1} has to be assigned to an A″ mode, ν_{12}, δ_{as}(NSF$_2$), because of the band contour having 18.5 cm^{-1} PR. The low Raman depolarization ratio contradicts this assignment, but for a weak Raman band like this one, the estimation of depolarization ratios contains large errors. The assignments of the remaining A′ bending modes are as follows: ν_6, 648 cm^{-1}, antisymmetric bend of NSF$_1$ angles; ν_7, 572 cm^{-1}, SF$_4$ wagging; ν_9, 340 cm^{-1}, SNF$_3$ bending mode; ν_{10}, 272 cm^{-1}, symmetric bend of equatorial NSF$_2$ angles. All these A′ vibrations show strong or medium IR absorptions with A′$_\parallel$ band contours and P and R branch separations of 14.5 cm^{-1}. The according Raman bands are polarized. There remains one fairly strong and polarized Raman band at 491 cm^{-1}, which is assigned to the symmetric axial NSF$_1$ bending vibration, ν_8. Except for the bands at 2270 and 1375 cm^{-1}, all features above 1126 cm^{-1} can be explained as combination bands and overtones containing at least one of the strong fundamentals. No restrictions on their activity in the IR exist from symmetry considerations of the point group C_s. A band at 2270 cm^{-1} is certainly due to an unknown NCO impurity because it occurs with variable intensity in different preparations. The band at 1375 cm^{-1} as well as weak peaks around 800 cm^{-1} coincide with the strongest bands of OSF$_4$,[29] and the sample is very likely to contain small amounts of OSF$_4$. All strong and medium IR absorptions below 1000 cm^{-1} have been assigned to funda-

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(32) (a) The reaction of FN═SF$_4$ with AsF$_5$ and SbF$_5$ may be similar to CF$_2$═NF.[32b] The latter forms a simple adduct with AsF$_5$ and polymerizes with SbF$_5$. The explosive reaction of FN═SF$_4$ with SbF$_5$ may therefore be due to an explosive polymerization. (b) Chang, S. C.; DesMarteau, D. D., unpublished results.

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Table III. Infrared and Raman Spectra of $FN{=}SF_4$ and Similar Compounds[a]

$SF_4{=}NF$					$SF_4{=}CH_2$[34]		OSF_4[29]		SF_4[40]
IR (gas)		Raman (liquid)							
ν, cm^{-1}	$\Delta\nu$(PR), cm^{-1}	$\Delta\nu$, cm^{-1}	depol ratio[c]	assignt	IR (gas) ν, cm^{-1}	Raman (liquid) $\Delta\nu$, cm^{-1}	IR (gas) ν, cm^{-1}	Raman (gas) $\Delta\nu$, cm^{-1}	IR (gas) ν, cm^{-1}
1126 s	*b*	1125 m	0.67	ν_1	1157 s	1149 s	1380 vs	1380 w	
929 vs	14.0	933 sh	dp	ν_{11}	760 s		926 s	924 w	867
870 vs	9.5	870 sh	dp	ν_2	818 vs		819 vs	820 sh	730
		850 m	0.43	ν_3					
757 s	14.5	754 s	0.03	ν_4		739 vs	796 m	795 vs	892
700 vw	*b*	697 w	p	ν_5	647 w	656 w	588 mw	587 m	558
648 s	14.5	644 s	0.18	ν_6	676 ms	684 vw	639 ms	640 sh	
594 m	23.0	591 w	p	ν_{12}	604 w	590 m	560 ms		
572 m	15.0	569 w	0.55	ν_7	565 ms	566 w	567 ms	566 m	475
		491 s	0.17	ν_8	509 mw	502 vw		174 w	228
479 w	18.5	476 m	0.75	ν_{13}	457 mw	449 ms	270 vw	265 w	353
340 m	14.5	341 w	0.19	ν_9	(1307 m)				
		316 w	0.74	ν_{14}		207 s	(475 calcd)		(437 calcd)
272 m	14.5	271 m	0.37	ν_{10}	298 w	298 w	447 vvw	455 vw	532
		140 m	0.75	ν_{15}		(430 vw)			
2050 w				$\nu_1 + \nu_{11}$					
1877 w				$\nu_1 + \nu_4$					
1792 w				$\nu_2 + \nu_{11}$					
1730 w				$2 \times \nu_2$					
1680 w				$\nu_4 + \nu_{11}$					
1620 m				$\nu_2 + \nu_4$					
1575 w	15			$\nu_6 + \nu_{11}$					
1515 m	10			$\nu_2 + \nu_6$					
1460 w				$\nu_1 + \nu_9, \nu_2 + \nu_{12}$					
1420 w				$\nu_8 + \nu_{11}$					
1350 w				$\nu_2 + \nu_8, \nu_2 + \nu_{13}$ $\nu_4 + \nu_{12}$					
1245 w				$\nu_9 + \nu_8, \nu_{11} + \nu_{14}$					
1025 w	*b*			$\nu_4 + \nu_{10}$					
987 w	14			$\nu_6 + \nu_9$					
		916 m	0.26	$\nu_6 + \nu_{10}$					
254 w				$\nu_{12} - \nu_9$					

[a] s, m, w, v, sh, and br stand for strong, medium, weak, very, shoulder, and broad, respectively. [b] PQR structure not resolved or hidden by overlapping bands. [c] p or dp when depolarization ratio was not measured quantitatively. Additional bands due to impurities: 2270 m IR, NCO; 822 w IR; 800 w IR, 790 vw R, OSF_4.

Table IV. Internal Valence Coordinates of $FN{=}SF_4$

coordinate	no.	description	coordinate[a]	no.	description
ΔR	1	SN stretch	$\Delta\alpha/(RS)^{1/2}$	7	SNF_3 bend
ΔS	2	NF_3 stretch	$(\Delta\beta_1,\Delta\beta_2)/(RT)^{1/2}$	8, 9	NSF_1 bend
ΔT_1, ΔT_2	3, 4	SF_1 stretch	$(\Delta\gamma_1,\Delta\gamma_2)/(RU)^{1/2}$	10, 11	NSF_2 bend
ΔU_1, ΔU_2	5, 6	SF_2 stretch	$\Delta\delta/T$	12	F_1SF_1 bend
			$\Delta\epsilon/U$	13	F_2SF_2 bend
			$(\Delta\psi_1,\Delta\psi_2,\Delta\psi_3,\Delta\psi_4)/(TU)^{1/2}$	14–17	F_1SF_2 bend
			$\Delta\tau$	18	torsion[b]

[a] Bending coordinates normalized to adjacent bond lengths: R, S, T, and U for SN, NF_3, SF_1, and SF_2 bond lengths, respectively. [b] Orientation of SNF_3 plane with respect to SF_4 group.

mentals in the preceding paragraph, and there are only two weak IR absorptions in this part of the spectrum which have to be assigned to combinations $\nu_6 + \nu_9$ at 987 cm^{-1} and $\nu_{12} - \nu_9$ at 254 cm^{-1}. For non-resonance Raman spectra only fundamentals should be observed in the absence of Fermi resonances. In general agreement with this rule there is only one of the observed weak bands, which has to be assigned to a combination, $\nu_6 + \nu_{10}$ (916 cm^{-1}). The weak Raman intensities around 800 and 250 cm^{-1} correspond to the strongest bands of OSF_4,[29] but all the impurity bands discussed above are of low intensity and the purity of the sample is estimated greater than 95%.

All of the above fundamentals and the overtones and combination bands along with their assignments are collected in Table III together with the spectra of the related molecules SF_4, OSF_4, and $CH_2{=}SF_4$ taken from the literature. There is in general not only a striking resemblance of the frequency and intensity patterns of the spectra of the four compounds compared here but also the assignments are in good agreement. Some discrepancies remain with regard to the SF_4 twist mode, the axial and equatorial SF_2 scissor, and the low frequency of the antisymmetric SF_2 (equatorial) stretch of $CH_2{=}SF_4$.

Normal-Coordinate Analysis of $FN{=}SF_4$. A normal-coordinate analysis of $FN{=}SF_4$ was performed in order to get information on the NS bond properties and at the same time to check the assignment and obtain a more detailed description of the vibrational modes. Six bond stretches, 11 bond angle deformations, and one torsional motion are necessary to describe the vibrations of the molecule (see Table IV). From these 18 internal coordinates, 18 symmetry coordinates are constructed of which 13 belong to spcies A′ and 5 to species A″ of point group C_s. Three redundant coordinates have to be removed from species A′. Both the triples no. 8, no. 9, no. 12 and no. 10, no. 11, no. 13 define three angles in a plane and therefore are linear dependent. The third of the redundancies involves all of the 10 angles around the sulfur atom.

Table V. Internal Symmetry Coordinates

species	description of coordinate	normalization factors	species of XSF_4 $(C_{2v})^a$	IR and Raman^b	
				C_s	C_{2v}
A′	$S_1 = \Delta R$		A_1	A, pol	A, pol
A′	$S_2 = A(\Delta T_1 - \Delta T_2)$	$A = 0.7071$	B_1	A, pol	A, dep
A′	$S_3 = \Delta S$		(B_1)	A, pol	A, dep
A′	$S_4 = A(\Delta U_1 + \Delta U_2)$	$A = 0.7071$	A_1	A, pol	A, pol
A′	$S_5 = A(\Delta T_1 + \Delta T_2)$	$A = 0.7071$	A_1	A, pol	A, pol
A′	$S_6 = A(1.02\Delta\beta_1 - \Delta\beta_2)$	$A = 0.7007$	B_1	A, pol	A, dep
A′	$S_7 = B'(\Delta\psi_1 + \Delta\psi_2) - B''(\Delta\psi_3 + \Delta\psi_4)$	$B' = 0.502$, $B'' = 0.488$	B_1	A, pol	A, dep
A′	$S_8 = C(\Delta\beta_1 + 1.02\Delta\beta_2) - D(\Delta\gamma_1 + \Delta\gamma_2) - E(\Delta\delta) + F(\Delta\epsilon) - G(\Delta\psi_1 + \Delta\psi_3 + \Delta\psi_4)$	$C = 0.3513, D = 0.0014, E = 0.7245, F = 0.0030, G = 0.2365$	A_1	A, pol	A, pol
A′	$S_9 = \Delta\alpha$		(B_1)	A, pol	A, dep
A′	$S_{10} = -K(\Delta\beta_1 + 1.02\Delta\beta_2) + L(\Delta\gamma_1 + \Delta\gamma_2) + M(\Delta\delta) - N(\Delta\epsilon) - O(\Delta\psi_1 + \Delta\psi_2 + \Delta\psi_2 + \Delta\psi_4)$	$K = 0.011, L = 0.4069, M = 0.219, N = 0.8164, O = 0.197$	A_1	A, pol	A, pol
A″	$S_{11} = A(\Delta U_1 - \Delta U_2)$	$A = 0.7071$	B_2	A, dep	A, dep
A″	$S_{12} = A(\Delta\gamma_1 - \Delta\gamma_2)$	$A = 0.7071$	B_2	A, dep	A, dep
A″	$S_{13} = B(\Delta\psi_1 - \Delta\psi_2 - \Delta\psi_3 + \Delta\psi_4)$	$B = 0.5$	B_2	A, dep	A, dep
A″	$S_{14} = B(\Delta\psi_1 - \Delta\psi_2 + \Delta\psi_3 - \Delta\psi_4)$ ("twist")	$B = 0.5$	A_2	A, dep	IA, dep
A″	$S_{15} = \Delta\tau$ ("tors")		(A_2)	A, dep	IA, dep

[a] Values in parentheses not present in OSF_4 and related to CH_2 group in CH_2SF_4. [b] A, IA, pol, and dep stand for IR active, IR forbidden, RA polarized and RA depolarized, respectively.

The zero coordinates constructed after the method of ref 12 are

$$\text{zero}_1 = 0.5672\Delta\beta_1 + 0.5867\Delta\beta_2 + 0.5691\Delta\delta$$

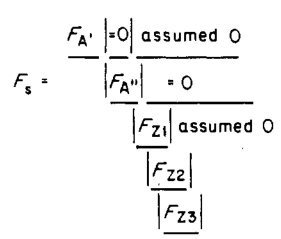
$$\text{zero}_2 = 0.5804\Delta\gamma_1 + 0.5804\Delta\gamma_2 + 0.5712\Delta\epsilon$$

$$\text{zero}_3 = 0.1885\Delta\beta_1 + 0.1920\Delta\beta_2 + 0.0161(\Delta\gamma_1 + \Delta\gamma_2) - 0.3888\Delta\delta - 0.0326\Delta\epsilon + 0.4374(\Delta\psi_1 + \Delta\psi_2) + 0.4429(\Delta\psi_3 + \Delta\psi_4)$$

For the set of independent symmetry coordinates obtained by orthogonalization of the **U** matrix and used for the normal-coordinate analysis, see Table V. A symmetry force field has been computed with the eigenvector method[13-15] and with some of the off diagonal elements constrained to zero. The elements of the symmetry force field which are representing the three redundant coordinates are indeterminate at this stage of approximation. The diagonal **F** matrix terms for coordinates zero_1, zero_2, and and zero_3 were estimated by comprison with related diagonal terms of the A′ block

$$F_{\text{zero}_1} \approx 2F_{8,8} \qquad F_{\text{zero}_2} \approx 2F_{10,10} \qquad F_{\text{zero}_3} \approx 0.8F_{7,7}$$

Back-transformation of the symmetrized **F** matrix into the space of internal coordinates was performed by applying the relation $\tilde{\mathbf{U}}\cdot F_s\cdot\mathbf{U} \rightarrow F_{\text{int}}$, with



The resulting set of general valence force constants is given as solution I in Table VI. It provides the set of approximate force constants to enter into Schachtschneider's FPERT[16] refinement program. This set of force constants was then refined in successive steps in order to reproduce the 15 frequencies of the molecule: step 1, refinement of idagonal terms; step 2, $F(SF_1')$ eliminated by application of Badger's rule on $F(SF_1')/F(SF_1)$ using the bond lengths $r_{SF_1} = 1.615$ Å and $r_{SF_1}' = 1.535$ Å with $F(SF_1')/F(SF_1 = 1.09$; step 3, to $n - 1$: refinement of sets of 6–10 off-diagonal terms (interaction constants); step n, final refinement of diagonal terms.

The solution thus achieved is tabulated in Table VI as solution II. Neglection of all of the off diagonal **F** matrix elements smaller than 0.08 mdyn Å^{-1} and refinement of the remaining set in the same way as above yields solution III of Table VI. It should be pointed out at this place that physical significance of the small off diagonal **F** matrix elements is very doubtful, but they are of great importance numerically for the accurate reproduction of the frequencies. Solution II is therefore the preferred set of force constants.

The force field given solution II of Table VI gives an excellent reproduction of the frequencies. In Table VII the calculated and observed frequencies are compared and the potential energy distribution of solution II is given both for symmetry coordinates and internal coordinates. The PED in symmetry coordinates shows that the assignment was not scrambled during the numerical procedure. Many of the vibrations are quite characteristic with the exception of ν_6 which carries only 37% of S_6 character. This result is somewhat surprising because the assignment (Table III) is very consistent throughout the series $FN{=}SF_4$, $CH_2{=}SF_4$, and OSF_4. The same is valid for ν_7, with which it could be interchanged.

Discussion of the force constants as to their relation with molecular properties is confined to the primary constants of bond strength coordinates. The force constant of 6.58 mdyn Å^{-1} for f(SN) gives strong evidence for multiple bond character of the SN bond. With Siebert's formula[41] the bond order of this bond is about 1.6, showing a similar double-bond character as for the CS bond of methylene sulfur tetrafluoride. Though the force constants of SF_1, SF_1', and SF_2, bond stretches were initially treated as independent parameters, already in solution I $f(SF_1')$ is greater than $f(SF_1)$, as their bond lengths would require, but $f(SF_2)$, which should be intermediate between $f(SF_1)$ and $f(SF_1')$, has the highest value of these three force constants. When $f(SF_1')$ was constrained to $1.09f(SF_1)$ in order to hold Badger's rule,[41a] $f(SF_2)$ also changed its value and dropped to the expected range (4.58 mdyn Å^{-1}). The force constant of the equatorial bond stretch then compares very well with the value reported for CH_2SF_4.[34]

Structure of $FN{=}SF_4$. The procedure for determining molecular geometries by joint analysis of electron diffraction and spectroscopic data have been described in the literature.[42] The harmonic vibrational corrections for the rotational con-

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Table VI. Internal Valence Force Field for FN=SF_4

			FN=SF_4			
no.	description	soln I	soln II	soln III	CH_2SF_4[34]	O=SF_4[29]
			Diagonal Terms			
1	$f(\mathrm{SN})$	6.69	6.58	6.52		
2	$f(\mathrm{NF_3})$	3.96	3.85	3.91		
3	$f(\mathrm{SF_1})$	4.62	4.49	4.37	4.31	3.54
3a	$f(\mathrm{SF_1'})$	4.67	4.89	4.76		
4	$f(\mathrm{SF_2})$	4.97	4.58	4.55	4.55	5.68
5	$f(\mathrm{SNF_3})$	0.72	0.860	0.871		
6	$f(\mathrm{NSF_1})$	1.37	1.54	1.56		
6a	$f(\mathrm{NSF_1'})$	1.35	0.883	0.827		
7	$f(\mathrm{NSF_2})$	0.57	0.625	0.621		
8	$f(\mathrm{F_1SF_1'})$	0.72	1.43	1.34	0.510	
9	$f(\mathrm{F_2SF_2})$	0.36	0.242	0.258	0.243	
10	$f(\mathrm{F_1SF_2})$	0.83	0.918	0.953	1.41	
10a	$f(\mathrm{F_1'SF_2})$	0.832	0.726	0.706		
11	$f(\mathrm{NF_3}$,“tors”$)$	0.0144	0.0145	0.0148		
			Stretch–Stretch Interactions			
12	$f(\mathrm{SN,NF_3})$	0.66	0.674	0.7038		
13	$f(\mathrm{SN,SF_1})$	0.068	−0.053			
13a	$f(\mathrm{SN,SF_1'})$	0.068	0.008			
14	$f(\mathrm{SN,SF_2})$	0.619	0.639	0.673		
15	$f(\mathrm{NF_3,SF_1})$	−0.094	−0.084	−0.038		
15a	$f(\mathrm{NF_3,SF_1'})$	0.126	0.123	0.204		
16	$f(\mathrm{NF_3,SF_2})$	0.160	0.160	0.225		
17	$f(\mathrm{SF_1,SF_1'})$	0.814	0.784	0.849	1.11	0.28
18	$f(\mathrm{SF_2,SF_1})$	−0.063	−0.060			
18a	$f(\mathrm{SF_2,SF_1'})$	0.067	1.1(0.060)			
19	$f(\mathrm{SF_2,SF_2})$	−0.316	−0.271	−0.217	0.384	0.27
			Stretch–Bend Interactions			
20	$f(\mathrm{NF_3,SNF_3})$	−0.013	−0.013			
21	$f(\mathrm{NF_3,NSF_1})$	−0.604	−0.608	−0.608		
21a	$f(\mathrm{NF_3,NSF_1'})$	0.579	0.574	0.574		
22	$f(\mathrm{NF_3,F_1SF_2})$	±0.034	±0.31			
23	$f(\mathrm{SF_{ax},NSF_{ax}})$	0.316	0.315	0.315		
23a	$f(\mathrm{SF_{ax}',NSF_{ax}})$	−0.327	−0.05(0.315)			
24	$f(\mathrm{SF_1,F_1SF_1'})$	0.016	0.033			
25	$f(\mathrm{SF_1,F_1SF_2})$	0.127	−1.1(0.115)	−1.1(0.108)		
25a	$f(\mathrm{SF_1',F_1SF_2})$	−0.115	−0.115	0.108		
26	$f(\mathrm{SF_2,SNF_3})$	0.043	0.050	0.087		
27	$f(\mathrm{SF_2,NSF_2})$	−0.115	−0.114	−0.111		
28	$f(\mathrm{SF_2,F_1SF_1'})$	0.102	0.101	0.101		
29	$f(\mathrm{SF_2,F_2SF_2})$	0.019	0.062			
30	$f(\mathrm{SF_2,F_1SF_2})$	0.084	1.3(0.062)			
30a	$f(\mathrm{SF_2,F_1'SF_2})$	0.062	0.062			
			Bend–Bend Interactions			
31	$f(\mathrm{SNF_3,NSF_1})$	±0.326	±0.327	0.356		
32	$f(\mathrm{NSF_1,NSF_1'})$	−0.451	−0.543	−0.604		
33	$f(\mathrm{NSF_1,F_1SF_1'})$	0.17	0.24(1.43)	0.24(1.34)		
34	$f(\mathrm{NSF_1,F_2SF_2})$	0.013				
35	$f(\mathrm{NSF_1,F_1'SF_2})$	0.055	0.027			
35a	$f(\mathrm{NSF_1',F_1SF_2})$	0.062	1.1(0.027)			
36	$f(\mathrm{NSF_2,NSF_2})$	−0.128	−0.136	−0.141		
37	$f(\mathrm{NSF_2,F_2SF_2})$	0.078	0.22(0.242)			
38	$f(\mathrm{NSF_2,F_1SF_1'})$	0.014	0.015			
39	$f(\mathrm{NSF_2,F_1'SF_2})$	0.015	0.016			
39a	$f(\mathrm{NSF_2,F_1SF_2})$	0.017	1.1(0.016)			
40	$f(\mathrm{F_1SF_1',F_2SF_2})$	−0.029	−0.034			
41	$f(\mathrm{F_1SF_1',F_1SF_2})$	−0.054	−0.1(1.43)	−0.1(1.34)		
42	$f(\mathrm{F_1SF_2,F_1SF_2})$	0.077	1.1(0.064)			
42a	$f(\mathrm{F_1'SF_2,F_1'SF_2})$	0.079	1.1 (0.064)			
42b	$f(\mathrm{F_1SF_2,F_1'SF_2})$	−0.064	−0.064			
42c	$f(\mathrm{F_1SF_2,F_1'SF_2})$	−0.120	−0.109	−0.112		

stants $\Delta B^i = B^i_0 - B^i_z$ (Table I and for the interatomic distances $\Delta r = r_a - r_\alpha{}^\circ$ (Table VIII) where calculated with the program NORCOR.[43] Error limits for the B^i_z constants are increased by the uncertainties in ΔB^i which were estimated to be 10% of the corrections. Molecular intensities were calculated with scattering amplitudes and phases of ref 44, and a diagonal weight matrix was applied to the molecular intensities.[8] The relative weight of electron diffraction and microwave data was adjusted until the rotational constants were reproduced within their estimated error limits (Table I). The only geometric constraints is planarity of the N=S$(F_2)_2$ entity. Attempts to relax this constraint resulted in deviations from planarity which were smaller than the standard deviations (about 0.8°). Some vibrational amplitudes were grouped together on the basis of the spectroscopic values. For the bonded distances the ratios

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Table VII. Fundamental Frequencies and Potential Energy Distribution[a]

mode	frequencies, cm^{-1} soln I	 soln II	 soln III	 obsd	PED (soln II),[b] %	PED (soln II),[c–e] %
A′	1126.6	1126.0	1126.0	1126	80 S1	$80f(SN)$
	870.0	870.0	872.0	870	69 S2 + 17 S7	$106f(SF_{ax}) + 13f(NSF_1) + 13f(F_1'SF_2)$
	850.0	850.0	849.5	850	60 S3 + 25 S6 + 13 S9	$82f(NF_3) + 30f(SNF_3) + (32 + 16)f(NSF_1)$
	754.3	753.8	754.8	754	13 S3 + 55 S4 + 14 S8	$63f(SF_2) + 14f(NF_3) + 12f(F_1SF_2)$
	697.0	696.8	692.9	697	97 S5	$84f(SF_{ax})$
	646.1	645.9	641.5	646	27 S4 + 37 S6 + 22 S7	$27f(SF_2) + (21 + 6)f(NSF_1) + (11 + 4)f(F_1SF_2)$
	571.8	572.7	572.6	572	23 S2 + 49 S7 + 10 S8	$21f(SF_{ax}) + (9 + 27)f(F_1SF_2)$
	491.1	490.0	489.7	490	31 S6 + 49 S8	$44f(NSF_1') + 20f(F_1SF_1') + (22 + 3)f(F_1SF_2)$
	327.3	339.7	333.4	340	10 S1 + 13 S8	$63f(SNF_3)$
	278.5	272.1	271.8	272	10 S9 + 86 S10	$69f(NSF_2) + 31f(F_2SF_2)$
A″	929.0	929.1	928.9	929	69 S11 + 26 S12	$69f(SF_2) + 24f(NSF_2)$
	594.2	593.8	593.9	594	29 S11 + 66 S12	$25f(SF_2) + 52f(NSF_2)$
	476.1	476.2	476.2	476	97 S13	$(68 + 35)f(F_1SF_2)$
	316.1	313.9	308.4	316	91 S14	$(36 + 72)f(F_1SF_2)$
	139.9	140.9	142.1	140	93 S15	$93f(NF_3$ torsion)

[a] Only contributions greater than 10% are included in the table. [b] PED in terms of symmetry coordinates. [c] PED in terms of principal constants of the internal valence force field. [d] Where two numbers are given, one refers to the F_1 part and one to the F_1' part of the molecule. [e] No distinction between $f(SF_1)$ and $f(SF_1')$ can be made.

Table VIII. Vibrational Amplitudes from Electron Diffraction and Spectroscopic Data and Harmonic Vibrational Corrections (Å) (See Figure 2 for Atom Numbering)

	vibrational amplitudes ED	 spectr	$r_a - r_\alpha^\circ$
S=N	0.037 (6)[a]	0.040	0.0007
$S-F_2$		0.043	0.0016
$S-F_1$	0.040 (6)[a]	0.044	0.0006
$S-F_1'$		0.043	0.0005
$N-F_3$	0.045 (6)[a]	0.048	0.0095
$F_2\cdots F_2$	0.074[b]	0.074	0.0005
$F_2\cdots F_1$		0.066	0.0011
$F_2\cdots F_1'$	0.065 (5)	0.062	0.0006
$N\cdots F_2$		0.058	0.0012
$N\cdots F_1$	0.059 (8)	0.053	0.0005
$N\cdots F_1'$		0.053	0.0013
$F_1\cdots F_1'$	0.052[b]	0.052	0.0002
$S\cdots F$	0.056[b]	0.056	0.0021
$F\cdots F_2$	0.097[b]	0.097	−0.0015
$F\cdots F_1$	0.090[b]	0.090	0.0013
$F\cdots F_1'$	0.059	0.059	0.0009

[a] Ratios between these amplitudes are fixed to the spectroscopic ratios. [b] Value not refined.

between various amplitudes were constrained to the spectroscopic ratios. Amplitudes which are badly determined by the electron diffraction experiment were not refined in the least squares analysis. The refined vibrational amplitudes are listed in Table VIII together with the spectroscopic values. Error limits for geometric parameters are 2σ values and 3σ values for vibrational amplutides.

The geometric parameters obtained from the joint least-squares analysis for $FN{=}SF_4$ are compared to the results for $CH_3N{=}SF_4$[45] and SF_4[46] in Table IX. The rather long S=N bond is clearly in accord with the bond order of 1.6 calculated from the vibrational spectra. In related sulfur(VI) compounds such as $HN{=}SOF_2$[47] and $ClN{=}SOF_2$,[48] the S=N bond lengths are 1.466 and 1.484 Å, respectively. These values are probably typical for a bond order of ~2 and compare favorably with $CH_3N{=}SF_4$.[45] Clearly, more electronegative substituents on nitrogen result in a lengthening of the S=N bond. The NF bond is relatively short (NF_3 = 1.364 Å)[49] and is shorter than cis or trans N_2F_2.[50] However, there are no structural data for closely analogous sulfur(IV) or -(VI) imines containing an NF bond.

Table IX. Geometric Parameters for $FN{=}SF_4$, $CH_3N{=}SF_4$, and SF_4 (Å and Deg) (See Figure 2 for Atom Numbering)

	$FN{=}SF_4$[a]	$CH_3N{=}SF_4$[b]	SF_4[c]
S=N	1.520 (9)	1.480 (6)	
$S-F_2$	1.564 (5)	1.567 (4)	1.545 (3)
$S-F_1$	1.615 (7)	1.643 (4)	1.646 (3)
$S-F_1'$	1.535 (12)	1.546 (7)	
N–X[d]	1.357 (8)	1.441 (16)	
F_2SF_2	99.8 (0.3)	102.6 (0.2)	101.5 (0.5)
NSF_1	96.9 (0.4)	98.4 (0.4)	
NSF_1'	90.6 (0.5)	94.6 (0.4)	
F_1SF_1'	172.5 (0.7)	167.0 (0.6)	173.1 (0.5)
SNX	117.6 (1.2)	127.2 (1.1)	

[a] Electron diffraction and microwave data (r_{av} structure) from this work. [b] Electron diffraction and microwave data (r_{av} structure) from ref 45. [c] Microwave data (r_o structure) from ref 46. [d] X = F or C.

The rather large difference in the two axial SF bond distances is noteworthy. The axial sulfur–fluorine bond in proximity to the fluorine on nitrogen is longer. The corresponding ∠NSF is also significantly larger. These results, which are quite similar to those of $CH_3N{=}SF_4$,[45] imply that the formal pair of electrons on nitrogen is less repulsive than the bonding pair in the NF or NCH_3 bond. Perhaps this is to be expected based on the structures of OSF_4 and $CH_2{=}SF_4$. Here the angles F_aSF_a are nearly ~164 and 170°, respectively, and the angles F_eSF_e are ~115 and 97°.[35] It has been concluded by ab initio calculations that the π bond between oxygen and sulfur has large contributions in both the axial and equatorial planes, whereas the π bond in $CH_2{=}SF_4$ is mainly in the equitorial plane.[35] Thus for $FN{=}SF_4$, it seems reasonable to assume a bonding model similar to that of $CH_2{=}SF_4$, with the distortion arising from the presence of a single NF bond in the axial plane. Like $CH_2{=}SF_4$, $FN{=}SF_4$ would then have a high barrier to positional exchange via the Berry pseudorotation mechanism, in agreement with the NMR.[35] However, the structure of $CH_3N{=}SF_4$ is clearly very similar to that of $FN{=}SF_4$ and $CH_2{=}SF_4$ and the NMR of $CH_3N{=}SF_4$ indicates that postional exchange of fluorines is occurring at 22 °C.[1,27] It is not obvious why $CH_3N{=}SF_4$ is so

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different from $FN{=}SF_4$ and $CH_2{=}SF_4$ in this regard.

Acknowledgment. This research was supported by funds from Deutsche Forschungegemeinschaft (H.H.E.), the U.S. Army Research Office, and the National Science Foundation (D.D.D.). Miss B. Saul is acknowledged for obtaining the Raman and infrared spectra. D.D.D. also wishes to acknowledge Professor K. Seppelt for his assistance in this work and the Alexander von Humboldt Stiftung for a research fellowship.

Registry No. SF_5NClF, 74542-21-5; SF_5NHF, 74542-22-6; $FN{=}SF_4$, 74542-20-4; $SF_3{\equiv}N$, 15930-75-3; ClF, 7790-89-8; F_2, 7782-41-4; TFA, 76-05-1.

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Acylations of Pentafluorosulfanylamine, SF_5NH_2

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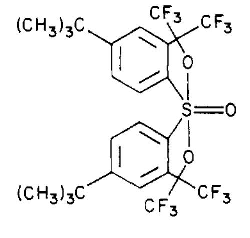
Received June 4, 1981

Acylation of SF_5NH_2 with select acyl halides has produced the corresponding *N*-pentafluorosulfanyl amides. The best yields were obtained in the reactions of acyl halides containing electron-deficient carbonyls. The first liquid pentafluorosulfanylcarbamyl derivative $SF_5NHC(O)F$ was prepared by the reaction of equimolar quantities of NSF_3, COF_2, and anhydrous HF. The reaction of SF_5NH_2 with $ClC(O)CF_2CF_2C(O)Cl$ produced not only the expected diamide $[SF_5NHC(O)CF_2]_2$ but also the novel cyclic imide $SF_5\overline{NC(O)CF_2CF_2C}(O)$. Other *N*-pentafluorosulfanyl amides were prepared from the reaction of SF_5NCO with suitable carboxylic acids. Several of the *N*-pentafluorosulfanyl amides synthesized were allowed to react with PCl_5 to produce the corresponding chloro imines. The compound $SF_5NHC(O)NHSF_5$ was also found to react with PCl_5 to produce the carbodiimide $SF_5N{=}C{=}NSF_5$. The products isolated were characterized by infrared and NMR spectroscopy, mass spectrometry, and elemental analysis.

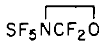
Introduction

In recent years there has been considerable interest in the synthesis and characterization of compounds containing five- and six-coordinate sulfur(VI).[1-11] This interest includes compounds containing sulfur as the central atom surrounded by five or six ligands as well as those employing six-coordinate sulfur as a functional group (e.g., the pentafluorosulfanyl group, SF_5).



$SF_4{=}NCH_3$ SF_5N

$SF_4{=}NF$



$SF_4{=}CH_2$ SF_5OH

Compounds containing the pentafluorosulfanyl group are of particular interest since they often possess the advantageous properties of the parent compound sulfur hexafluoride. These properties include a high group electronegativity, a large steric bulk (greater than than of F or CF_3), a nonfluctional hexacoordinate stereochemistry, and high thermal and hydrolytic stability.

While investigations of carbon- and oxygen-substituted SF_6 derivatives have been carried out in other laboratories, we have for sometime been investigating those compounds containing the *N*-pentafluorosulfanyl linkage. Along these lines we wish to report our results in the synthesis and characterization of several new $SF_5N<$ compounds as well as an alternate synthesis of several previously reported $SF_5N<$ compounds. Three types of reactions have been investigated: the acylation of SF_5NH_2, the reaction of SF_5NCO with carboxylic acids, and the conversion of NSF_5 amides to chloro imines by reaction with PCl_5.

Prior to this investigation two methods for the synthesis of compounds containing pentafluorosulfanyl-nitrogen-carbon linkages had been reported. The first, reported by Tullock et al., involves the photolytically induced free radical reaction between SF_5Cl and selected nitriles.[12] This reaction is limited in scope and provides only low yields of these materials. The chloro pentafluorosulfanylimines produced can further react to give secondary amines or alternate imines as shown by the two examples in Scheme I.[12,13]

Scheme I

$$SF_5Cl + R_fCN \xrightarrow{h\nu} SF_5N{=}C(Cl)R_f \qquad (1)$$

$$SF_5N{=}C(Cl)R_f + HF \xrightarrow{NaF} SF_5NHCF_2R_f \qquad (2)$$

$$SF_5N{=}C(Cl)R_f + NaN_3 \rightarrow SF_5N{=}C(N_3)R_f \qquad (3)$$

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