a larger decrease in entropy. An additional factor which contributes to a lower change in entropy for the chloroform–tetrahydrofuran system is the availability of two unshared pairs of electrons in tetrahydrofuran. Since there is available only one pair of electrons in triethylamine, the association is more probable in the case of tetrahydrofuran. The change of free energy for the association of chloroform and tetrahydrofuran is thus larger than that of the association of chloroform and triethylamine.

The Microwave Spectrum and Structure of NSF[1a]

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The microwave spectrum of the compound reported to be SNF was investigated in order to remove the uncertainty regarding its structure. The compound was found, contrary to previous notions, to have the (bent) structure $N \equiv S - F$ with the molecular dimensions: $d_{SF} = 1.646 \pm 0.01$ Å., $d_{SN} = 1.446 \pm 0.01$ Å. and $\angle NSF = 116°52' \pm 15'$. These dimensions are compatible with the force constants of the bonds as determined from previous infrared work. The quadrupole coupling constants are $eq_aQ = -1.66 \pm 0.05$ Mc. and $\eta = +5.86 \pm 0.05$. The hydrolysis of NSF to give HNSO was also confirmed.

Introduction

In 1955, Glemser, Schröder and Haeseler reported the preparation of a mixture of SNF and SN_2F_2 by the action of AgF_2 on S_4N_4 but were unable to obtain pure SNF^2; in the following year, the preparation of the isomer NSF was reported as arising from the thermal decomposition of SN_2F_2.[2b] NSF was described as being quite stable with a boiling point of 4.8° and a melting point of −79°. The hydrolysis of NSF was interpreted as favoring the structure $N \equiv S - F$. In 1961, Glemser and Richert reported the isolation of SNF and gave its boiling point as $0.4 \pm 2°$ and its melting point as −89°.[3] In addition they obtained the infrared spectrum and the fluorine nuclear magnetic resonance spectrum of SNF and interpreted their results in favor of the structure $S = N - F$.[4] However, they were unable to repeat the preparation of SN_2F_2 and were led to the conclusion that this compound did not exist. Since NSF was reported as arising from the decomposition of SN_2F_2, its existence would also be in some doubt.

Also in 1961, Rogowski, presumably working with a sample supplied by Glemser,[5] determined the structure of SNF by means of electron diffraction studies.[6] He obtained the molecular parameters: $d_{SN} = 1.62 \pm 0.03$ Å., $d_{NF} = 1.42 \pm 0.03$ Å. and $\angle SNF = 122 \pm 3°$. In their interpretation of the infrared spectrum of SNF based on the $S = N - F$ model, Richert and Glemser calculated the force constants of the SN and the NF bonds. If one then uses Badger's rule[7] to estimate the bond distances from the force constants, the following bond distances are obtained: $d_{SN} = 1.45$ Å. and $d_{NF} = 1.63$ Å. The results of the infrared work and the electron diffraction work appear to be incompatible.[8] Furthermore, Glemser and Richert reported the preparation of SNF as also arising from the thermal decomposition of $S_4N_4F_4$ where the fluorine atoms are bonded

to the sulfur atoms. One would expect NSF to be formed from such a decomposition. These anomalies plus the uncertainty concerning the existence of NSF indicated that further studies of this system would be advisable.

Microwave spectroscopy is an ideal tool for dealing with systems which contain a number of compounds since the spectrum of each component of the mixture is quite distinct and separate from the spectrum of every other component. In addition, the microwave spectra of most of the side products have already been reported so transitions due to these species could easily be accounted for. As will be shown below, the compound claimed by Glemser and Richert to be SNF is in fact NSF and has the molecular parameters: $d_{SF} = 1.646$ Å., $d_{SN} = 1.446$ Å. and $\angle NSF = 116°52'$.

Description of the Experiments

The Preparation of NSF.—NSF is formed in the reaction of AgF_2 with S_4N_4 in an inert solvent. The procedure followed was that outlined by Glemser and Richert.[3] The crude NSF was purified somewhat by the use of a low temperature fractional distillation apparatus. The sample thus obtained consisted of roughly 50% NSF, the major impurities being CCl_3F, SO_2, HNSO and SOF_2. The composition of the sample was determined from the mass spectrum, the infrared spectrum and the fluorine nuclear magnetic resonance spectrum.

The Microwave Spectrum of NSF.—The microwave spectrum of the impure sample was investigated using a conventional Stark modulated spectrometer. Some of the observed transitions were assigned to NSF by relating the intensity of the transition to the amount of NSF present in the sample as determined from the mass spectrum. Some of these transitions had resolvable fine structure which was attributed to the coupling of the spin of the nitrogen nucleus to the over-all rotation of the molecule by means of the electrical quadrupole moment of the nitrogen nucleus. For certain transitions, resolvable Stark effects were observed, and these observations led to an assignment of the microwave spectrum of the normal isotopic species of NSF. The assignment of the rotational transitions was based upon measurement of the quadrupole splitting, the observed Stark effect, and upon the agreement of the observed frequency with the values calculated from a fitted rigid asymmetric rotor model.

The quadrupole coupling constants

$$eq_aQ = \partial^2 V / \partial a^2$$

and

$$\eta = \frac{\partial^2 V / \partial b^2 - \partial^2 V / \partial c^2}{\partial^2 V / \partial a^2}$$

where a, b and c are coördinates located along the principal moments of inertia and V is the potential at the nitrogen nucleus due to all the external charge distribution, were calculated from

(1) (a) This research was supported by a grant extended to Harvard University by the Office of Naval Research. (b) NIH Fellow, 1959–1962.

(2) (a) O. Glemser, H. Schröder and H. Haeseler, Z. anorg. allgem. Chem., **279**, 28(1955); (b) O. Glemser and H. Haeseler, ibid., **287**, 54 (1956).

(3) O. Glemser and H. Richert, ibid., **307**, 313 (1961).

(4) O. Glemser and H. Richert, ibid., **307**, 328 (1961).

(5) O. Glemser, H. Richert and F. Rogowski, Naturwissenschaften, **47**, 94 (1960).

(6) F. Rogowski, Z. physik. Chem. (Frankfurt), **27**, 277 (1961).

(7) R. M. Badger, J. Chem. Phys., **3**, 710 (1935).

(8) Prof. R. M. Badger suggested to one of us that there seemed to be a discrepancy for this molecule.

TABLE I
THE CALCULATED AND OBSERVED ROTATIONAL TRANSITIONS OF NSF

$J_{K_-,K_+} \to J'_{K'_-,K'_+}$	$F \to F'$	ν, obsd., Mc.	ν, calcd., Mc.	$\Delta\nu$, Mc.
$0_{0,0} \to 1_{0,1}$	1 → 2	16,105.50	16,105.58	−0.08
	1 → 1	....	16,105.09	....
	0 → 1	....	16,105.33	....
$1_{0,1} \to 1_{1,0}$	2 → 2	42,324.46	42,324.38	− .08
	1 → 1	42,326.63	42,326.58	− .05
	2 → 1	42,326.11	42,326.09	− .02
	1 → 0	32,322.34	42,322.32	− .02
	1 → 2	42,324.94	42,324.88	− .06
	0 → 1	42,325.38	42,325.34	− .04
$1_{1,1} \to 2_{1,2}$	2 → 3	30,892.13	30,891.89	.32
	1 → 2 }	30,891.49	30,891.27 }	.31
	0 → 1 }		30,891.09 }	
$1_{0,1} \to 2_{0,2}$	2 → 3 }	32,179.27	32,179.72 }	− .41
	1 → 2 }		32,179.64 }	
	0 → 1	....	32,179.30	....
$1_{1,0} \to 2_{1,1}$	2 → 3	33,530.31	33,530.32	− .01
	1 → 2	....	33,529.91	....
	0 → 1	....	33,532.15	....
$1_{1,1} \to 2_{0,2}$	2 → 3	8,825.96	−8,825.83	− .13
	1 → 2	8,825.31	−8,825.20	− .11
	0 → 1	8,827.46	−8,827.32	− .14
	1 → 1	8,824.46	−8,824.30	− .16
	2 → 2	8,826.50	−8,826.41	− .09
$2_{1,2} \to 3_{0,3}$	3 → 4	8,472.23	8,473.64	−1.41
	2 → 3	8,473.42	8,474.79	−1.37
	1 → 2	8,471.52	8,472.87	−1.34
$3_{1,3} \to 4_{0,4}$	4 → 5	26,261.53	26,265.20	−3.67
	2 → 3	....	26,264.69	....
	3 → 4	26,262.69	26,266.46	−3.77
$1_{0,1} \to 2_{1,2}$	2 → 2	71,895.62	71,895.61	0.01
	2 → 1	....	71,898.46	
	1 → 2	71,896.10	71,896.10	.00
	1 → 1	71,898.93	71,898.94	− .01
	2 → 3 }	71,897.53	71,897.43 }	− .04
	0 → 1 }		71,897.70	
$2_{2,1} \to 3_{1,2}$	3 → 4 }		−72,740.80 }	
	2 → 3 }	72,713.61	−72,740.15 }	27.02
	1 → 2 }		−72,740.92 }	
$3_{2,2} \to 4_{1,3}$	4 → 5 }		−54,060.84 }	
	3 → 4 }	54,038 ± 2	−54,059.71 }	23 ± 2
	2 → 3 }		−54,061.12 }	
$4_{2,3} \to 5_{1,4}$	5 → 6	34,758.35	−34,774.75	16.40
	4 → 5	34,757.01	−34,773.43	16.42
	3 → 4	34,758.61	−34,775.04	16.43
$5_{2,4} \to 6_{1,5}$	5 → 6	14,896.43	−14,904.13	7.70
	6 → 7 }	14,897.89	−14,905.55 }	7.69
	4 → 5 }		−14,905.80 }	
$7_{2,6} \to 8_{1,7}$	7 → 8	26,439.41	26,458.99	−19.58
	8 → 9 }	26,437.85	26,457.52 }	−19.57
	6 → 7 }		26,457.32 }	
$6_{2,4} \to 7_{1,7}$	7 → 8	33,478.91	−33,492.10	13.19
	6 → 7	33,481.42	−33,494.56	13.14
	5 → 6	33,478.56	−33,491.75	13.19
$7_{2,5} \to 8_{1,8}$	7 → 8	24,681.70	−24,691.35	9.65
	8 → 9 }	24,678.78	−24,688.72 }	9.77
	6 → 7 }		−24,688.39 }	
$8_{2,6} \to 9_{1,9}$	8 → 9	17,427.95	−17,435.90	7.95
	9 → 10 }	17,424.86	−17,433.08 }	8.06
	7 → 8 }		−17,432.76 }	

$J_{K_-,K_+} \to J'_{K'_-,K'_+}$	$F \to F'$	ν, obsd., Mc.	ν, calcd., Mc.	$\Delta\nu$, Mc.
$9_{2,7} \to 10_{1,10}$	10 → 11	11,889.28	−11,898.49	9.21
	9 → 10	11,892.31	−11,901.51	9.20
	8 → 9	11,888.95	−11,898.19	9.24
$10_{2,8} \to 11_{1,11}$	11 → 12	8,221.14	−8,236.21	15.07
	10 → 11	8,224.42	−8,239.42	15.00
	9 → 10	8,220.82	−8,235.91	15.09
$13_{2,11} \to 14_{1,14}$	14 → 15	9,366.39	−9,445.34	78.95
	13 → 14	9,370.22	−9,449.07	78.85
	12 → 13	9,366.14	−9,445.07	78.93
$14_{2,12} \to 15_{1,15}$	14 → 15	13,921.73	−14,028.21	106.48
	13 → 14 }	13,917.70	−14,024.10 }	106.53
	15 → 16 }		−14,024.36 }	
$15_{2,13} \to 16_{1,16}$	15 → 16	20,477.47	−20,653.40	175.93
	16 → 17 }	20,473.40	−20,649.45 }	175.93
	14 → 15 }		−20,649.20 }	
$16_{2,14} \to 17_{1,17}$	17 → 18	29,003.32	−29,248.73	245.41
	16 → 17	29,007.37	−29,252.76	245.39
	15 → 16	29,003.06	−29,248.49	245.43
$9_{3,7} \to 10_{2,8}$	10 → 11 }		−36,407.54 }	
	9 → 10 }	36,366.81	−36,406.73 }	40.7
	8 → 9 }		−36,407.63 }	
$10_{3,8} \to 11_{2,9}$	10 → 11	16,079.34	−16,084.57	5.23
	11 → 12 }	16,080.37	−16,085.53 }	5.21
	9 → 10 }		−16,085.62 }	
$10_{3,7} \to 11_{2,10}$	11 → 12 }		−37,070.95 }	
	10 → 11 }	37,020.30	−37,071.57 }	51.17
	9 → 10 }		−37,071.89 }	
$12_{3,9} \to 13_{2,12}$	12 → 13	10,907.57	−10,924.69	17.12
	11 → 12 }	10,906.67	−10,923.76 }	17.13
	13 → 14 }		−10,923.83 }	
$14_{3,11} \to 15_{2,14}$	14 → 15	11,267.12	11,270.61	−3.49
	13 → 14 }	11,268.22	11,271.84 }	−3.58
	15 → 16 }		11,271.76 }	
$15_{3,12} \to 16_{2,15}$	15 → 16	20,421.55	20,424.34	−2.79
	16 → 17 }	20,422.82	20,425.67 }	−2.89
	14 → 15 }		20,425.75 }	
$16_{3,13} \to 17_{2,16}$	16 → 17	28,029.27	28,019.72	10.05
	17 → 18 }	28,030.78	28,020.72 }	10.01
	15 → 16 }		28,020.81 }	
$17_{3,14} \to 18_{2,17}$	17 → 18	33,901.19	33,862.03	39.16
	18 → 19 }	33,902.92	33,863.72 }	39.14
	16 → 17 }		33,863.82 }	
$15_{4,11} \to 16_{3,14}$	16 → 17 }		−32,503.02 }	
	15 → 16 }	32,425.85	−32,503.16 }	77.21
	14 → 15 }		−32,503.01 }	
$16_{4,12} \to 17_{3,15}$	17 → 18 }		−16,939.88 }	
	16 → 17 }	16,904.72	−16,940.06 }	35.22
	15 → 16 }		−16,939.87 }	
$18_{4,14} \to 19_{3,17}$	19 → 20 }		12,871.17 }	
	18 → 19 }	12,809.6	12,871.47 }	−61.8
	17 → 18 }		12,871.49 }	
$15_{4,12} \to 16_{3,13}$	15 → 16	20,649.27	−20,646.07	−3.20
	16 → 17 }	20,649.84	−20,646.60 }	−3.22
	14 → 15 }		−20,646.64 }	
$17_{4,14} \to 18_{3,15}$	17 → 18	20,661.14	20,863.57	−202.43
	18 → 19 }	20,660.37	20,862.83 }	−202.44
	16 → 17 }		20,862.78 }	

the $1_{0,1} \to 1_{1,0}$ and the $1_{0,1} \to 2_{1,2}$ transitions by fitting the observed splittings to the appropriate equations given by Townes and Schawlow.[9] (The sign of η should be reversed wherever it appears in eq. 6–22.) The coupling constants thus obtained are $eq_aQ = -1.66 \pm 0.05$ Mc. and $\eta = +5.86 \pm 0.05$.

Values of the rotational constants were obtained from the $0_{0,0} \to 1_{0,1}$, the $1_{1,1} \to 2_{1,2}$ and the $1_{0,1} \to 2_{1,2}$ transitions. From these constants and from the quadrupole coupling constants,

the microwave transitions for values of J from 0 to 20 were calculated using a program written for the IBM 7090 computer by Beaudet, Kirtman and Cahill.[10] The calculated and observed values for the assigned transitions are given in Table I. The calculated values are based on the rotational constants given in Table III. The values of the frequency differences are also included and are assumed to be due to centrifugal distortion effects. Although these differences appear in certain instances to be quite large, they are comparable in magnitude to those found in similar molecules such as SO_2 and OF_2.

(9) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p. 162.

(10) R. A. Beaudet, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1961, pp. V-1 to AI-13.
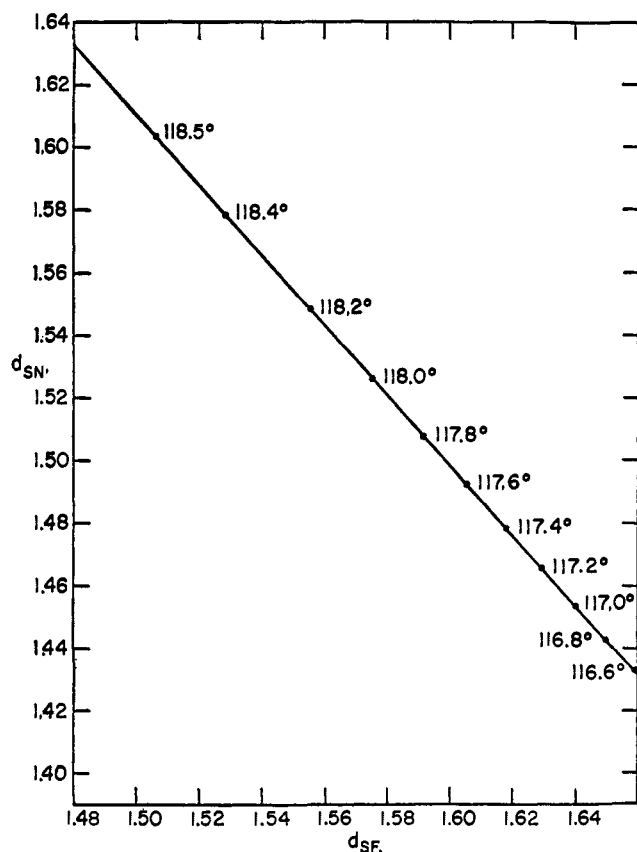
Fig. 1.—A plot of d_{SN} vs. d_{SF} for the NSF model to fit the rotational constants A = 49,717.84 Mc. and, B = 8,712.41 Mc.
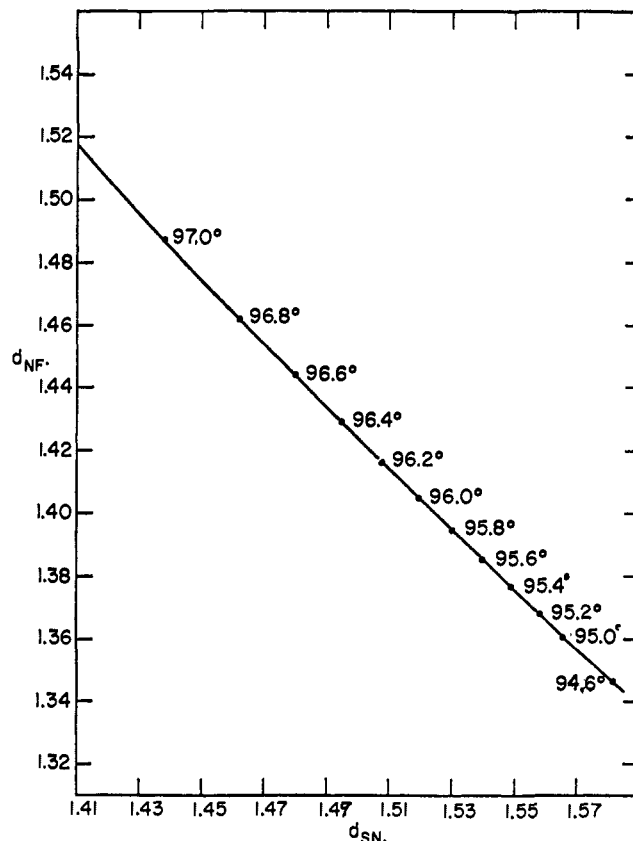

Fig. 2.—A plot of d_{SN} vs. d_{NF} for the SNF model to fit the rotational constants A = 49,717.84 Mc. and B = 8,712.41 Mc.

With the assignment of the rotational spectrum of the normal isotopic species, two independent rotational constants were obtained, the third constant being related to the other two by the planarity condition. Since only three parameters are needed to describe the structure of the NSF molecule, two of these parameters could be calculated as functions of the third by fitting two of the rotational constants. Thus, a plot was obtained of d_{SN} vs. d_{SF} assuming an NSF structure and of d_{NF} vs. d_{SN} assuming an SNF structure. These plots are shown in Fig. 1 and 2. It can be seen from Fig. 2 that the molecular distances for the SNF model are not in agreement with either the electron diffraction work or the bond distances given above as estimated from the SN and NF force constants.

The infrared spectrum and the fluorine nuclear magnetic resonance spectrum of the sample were measured and gave lines agreeing with the results reported by Glemser and Richert for SNF. Thus, the microwave spectrum which was assigned was due to the same substance which was studied by Glemser and Richert. Furthermore, the molecular weight measurements and the fluorine, sulfur and nitrogen determinations carried out by Glemser and Richert plus evidence from the mass spectrum show that the compound does have the empirical formula SNF. As pointed out above, the microwave results on the normal isotopic species are incompatible with the infrared results when an SNF model is assumed. Thus, it appears that the NSF model is the correct one.

In order to determine the structure of NSF unambiguously, it was necessary to assign the rotational spectrum of the ^{34}S species. Using the NSF model, a range of structural parameters was chosen which seemed most reasonable. Corresponding to the range in the dimensions, a range was obtained for each of the predicted transitions of the ^{34}S species. These regions were then searched for possible ^{34}S transitions. An assignment was made of a possible ^{34}S spectrum based on eleven observed transitions. These transitions were identified by their weak intensity, their frequency shift relative to the normal species, and their quadrupole hyperfine structure which should be similar to that for the corresponding transitions in the normal species. In no case could an alternative transition be assigned which had the proper quadrupole splittings and which occurred within 25 Mc. of the assigned transition.

The temperature dependence of the ratio of the intensity of the $8_{2,6} \rightarrow 9_{1,9}$ transition of the ^{34}S species to the intensity of the $5_{2,4} \rightarrow 6_{1,5}$ transition of the ^{32}S species was in accord with the assignment of the weaker line as a ^{34}S species.

The calculation of the rotational constants from the observed transitions was made difficult by the fact that many of the low J

ines observed for the normal species were shifted to frequency regions which could not be reached with the existing apparatus. Also, the ^{34}S, a-type transitions could not be seen because of their very low intensity. Therefore the calculation of the rotational constants had to be made using transitions which had shown rather appreciable centrifugal distortion corrections in the spectrum of the normal species. A first approximation would be to account for the distortion effects by assuming that the correction for a given transition of the ^{34}S species was the same as that for the corresponding transition in the normal species. A somewhat better estimate can be obtained by noticing that for certain R-branch series (for example, the $J_{2,J-1} \rightarrow (J + 1)_{1,J}$ series) the value of the centrifugal distortion correction divided by the frequency of the transition is a slowly varying function of J. Therefore, a slight improvement is made in correcting for centrifugal distortion effects by multiplying the centrifugal distortion correction of a given transition in the normal species by the ratio of the frequency of the transition in the ^{34}S species to the frequency of the transition in the normal species.

The calculated and observed transitions of the ^{34}S species are given in Table II. The quadrupole splittings of the calculated transitions were obtained using the quadrupole coupling constants of the ^{32}S species. The rotational constants, moments of inertia, and the inertial defects of the ^{32}S and the ^{34}S species are given in Table III.

The Hydrolysis of NSF.—In order to confirm the hydrolysis experiments carried out by Richert and Glemser, NSF was allowed to react with H_2O in the microwave absorption cell at $-78°$. The NSF transitions slowly disappeared and transitions due to cis-thionylimide, HNSO, were seen to appear. The hydrolysis of NSF to give HNSO was thus confirmed. The possibility of the formation of trans-thionylimide was not investigated.

Interpretation of the Experiments

With the assignment of both the ^{32}S and the ^{34}S species, it is possible to calculate the structure of NSF. The NSF model was found to be the correct one and has the molecular dimensions: d_{SF} = 1.646 ± 0.01 Å., d_{SN} = 1.446 ± 0.01 Å. and $\angle$NSF = 116°52' ± 15'. These dimensions are those which best fit the A and B rotational constants of the two isotopic species.

The exact meaning of these structural parameters is somewhat ambiguous, since precise information concerning the zero point vibrations and their effect on the

TABLE II

THE CALCULATED AND OBSERVED FREQUENCIES OF ROTATIONAL
TRANSITIONS OF $N^{34}SF$

$J_{K_-,K_+} \to$ $J'_{K_-',K_+'}$	$F \to F'$	ν, obsd., Mc.	ν, calcd., Mc.	$\Delta\nu$, Mc.
$1_{0,1} \to 1_{1,0}$	$1 \to 1$	40,945.44	40,945.90	−0.22
	$2 \to 1$		40,945.41	
	$1 \to 2$		40,943.70	
	$1 \to 2$	40,944.07	40,944.20	−0.12
	$0 \to 1$		40,944.66	
	$1 \to 0$	....	40,941.64	
$2_{1,2} \to 3_{0,3}$	$3 \to 4$	9,744.08	9,745.90	−1.82
	$2 \to 3$	9,745.12	9,747.04	−1.92
	$1 \to 2$	9,743.35	9,745.12	−1.77
$4_{2,3} \to 5_{1,4}$	$4 \to 5$	30,627.67	−30,642.07	14.40
	$5 \to 6$	30,629.01	−30,643.40	14.53
	$3 \to 4$		−30,643.68	
$5_{2,4} \to 6_{1,5}$	$5 \to 6$	10,747.13	−10,753.08	5.95
	$6 \to 7$	10,748.64	−10,754.50	5.99
	$4 \to 5$		−10,754.75	
$6_{2,5} \to 7_{1,6}$	$6 \to 7$	9,689.05	9,694.73	−5.68
	$7 \to 8$	9,687.58	9,693.29	−5.60
	$5 \to 6$		9,693.06	
$7_{2,6} \to 8_{1,7}$	$7 \to 8$	30,640.01	30,660.67	−20.66
	$8 \to 9$	30,638.50	30,659.20	−20.60
	$6 \to 7$		30,659.00	
$6_{2,4} \to 7_{1,7}$	$7 \to 8$	30,283.01	−30,293.20	10.19
	$6 \to 7$	30,285.51	−30,295.67	10.16
	$5 \to 6$	30,282.65	−30,292.85	10.20
$7_{2,5} \to 8_{1,8}$	$8 \to 9$	21,805.46	−21,812.11	6.65
	$7 \to 8$	21,808.20	−21,814.74	6.54
	$6 \to 7$	21,805.07	−21,811.78	6.71
$8_{2,6} \to 9_{1,9}$	$8 \to 9$	14,951.28	−14,956.02	4.74
	$9 \to 10$	14,947.94	−14,953.20	5.10
	$11 \to 12$		−14,952.88	
$9_{3,7} \to 10_{2,8}$	$9 \to 10$	29,140.12	−29,173.18	33.06
	$10 \to 11$	29,141.04	−29,174.00	33.00
	$11 \to 12$		−29,174.08	
$10_{3,7} \to 11_{2,10}$	$10 \to 11$	31,118.05	−31,162.14	44.09
	$11 \to 12$	31,117.39	−31,161.51	44.09
	$9 \to 10$		−31,161.45	

TABLE III

ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA[a] FOR $N^{32}SF$
AND $N^{34}SF$

$N^{32}SF$	$N^{34}SF$
A = 49,717.84 Mc.	A = 48,296.84 Mc.
B = 8,712.41	B = 8,701.32
C = 7,393.09	C = 7,352.77
I_a = 10.1680 Amu. Å.^{2}	I_a = 10.4672 Amu. Å.^{2}
I_b = 58.0242	I_b = 58.0982
I_c = 68.3789	I_c = 68.7538
$\Delta = I_c - I_a - I_b = 0.1867$ Amu. Å.^{2}	$\Delta = 0.1884$ Amu. Å.^{2}

[a] Conversion factor = 505,531 (Mc.)(Amu.)(Å.)^2.

molecular distances is not known. Furthermore, preliminary calculations on the centrifugal distortion effects have shown that the rotational constants for the rigid rotor model may have to be altered—A by possibly as much as 3 megacycles and B and C by as much as 1

megacycle. However, any refinements in the calculation of the structure should fall within the limits given above.

Glemser and Richert have also calculated force constants from their infrared work using an NSF model. The constants appropriate to the molecular dimensions calculated from the microwave spectrum are f_{SF} = 2.85 mdynes/Å. and f_{SN} = 10.69 mdynes/Å. It is interesting to see if these force constants are compatible with Badger's rule and the above structure.

Badger's rule states that the force constant for a given bond is related to the bond distance by the relation[7]

$$r_e = (C_{ij}/k)^{1/3} + d_{ij}$$

where r_e is the equilibrium internuclear distance in Ångstroms, k the force constant of the bond in megadynes/cm., and C_{ij} and d_{ij} are empirical constants which depend on the atoms i and j. These constants were evaluated for the SF bond using the force constants and bond distances in NSF_3,[11,12] SOF_2[13,14] and SO_2F_2,[15,16] and for the SN bond using force constants and bond distances in NSF_3[11,12] and SN.[17] The constants thus obtained are: $C_{SF}^{1/3} = 0.384$, $d_{SF} = 1.055$Å., $C_{SN}^{1/3} = 0.660$ and $d_{SN} = 0.673$ Å. and the calculated bond distances in NSF are: $r_{SN} = 1.445$ Å. and $r_{SF} = 1.639$ Å., which agree quite well with the bond distances calculated from the rotational spectra.

Conclusion

It has been shown that in the reaction of AgF_2 with S_4N_4 the major product, in addition to NSF_3, is NSF, a bent triatomic molecule with sulfur in the middle. A quantitative structure has been determined which is compatible with previous work on the infrared spectrum of this compound. The NSF molecule can be thought of as being derived from SF_4 with three of the fluorine atoms replaced by a triply bonded nitrogen atom. The SN distance in NSF is only slightly greater than the SN distance in NSF_3[12] and the SF distance in NSF is the same as the long SF distance in SF_4.[18] The SN bond is not cylindrically symmetric, for if it were, the quadrupole coupling constant η would be 1.437 instead of 5.86.

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