(27) Hariharan, P. C.; Lathan, W. A.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *14*, 385.
(28) Zurawski, B.; Ahlrichs, R.; Kutzelnigg, W. *Chem. Phys. Lett.* **1973**, *21*, 309.
(29) Lischka, H.; Köhler, H.-J. *J. Am. Chem. Soc.* **1978**, *100*, 5297.
(30) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290.
(31) Levin, N.; Hartung, W. "Organic Syntheses", Collect. Vol. III; Wiley: New York, 1955; p 152.
(32) Atkinson, J.; Csakvary, J. J.; Herbert, G. T.; Stuart, R. S. *J. Am. Chem. Soc.* **1968**, *90*, 498.
(33) The features assigned to be adiabatic IPs are assumed to be the first members of the resolved vibrational progressions. We recognize the difficulties in identifying the first member of a progression where the adiabatic ionization energy is significantly displaced from the vertical or most probably ionization energy. At the temperatures employed for these experiments, rotation energy is significant (e.g., 0.075 eV at 573 K), and many rotational levels will be populated. Selection rules depend on the electronic part of the wave function involved in the initial and final states, but for these systems where symmetry is low the transitions probably involve changes in rotational quantum numbers of 0 or ±1. We have chosen our adiabatic IPs to be the maxima of the resolved vibrational features, corresponding approximately to what would be a Q branch. This will be approximately the 0,0 ← 0,0 transition energy. The rotational energy will serve to broaden the band about this point. Accordingly, we feel that the instrumental line width is the chief source of error in the stated values for the adiabatic IPs, and have not attempted to otherwise account for the effects of rotational energy.
(34) Houle, F. A.; Beauchamp, J. L. *Chem. Phys. Lett.* **1977**, *48*, 457.
(35) Williams, J. M.; Hamill, W. H. *J. Chem. Phys.* **1968**, *49*, 4467.
(36) Lossing, F. P.; Semeluk, G. P. *Can. J. Chem.* **1970**, *48*, 955.
(37) Chupka, W. A.; Berkowitz, J. *J. Chem. Phys.* **1967**, *47*, 2921.
(38) Elder, F. A.; Giese, C.; Steiner, B; Inghram, M. *J. Chem. Phys.* **1962**, *36*, 3292.
(39) Dyke, J.; Jonathan, N.; Lee, E.; Morris, A.; Winter, M. *Phys. Scr.* **1977**, *16*, 197.
(40) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.
(41) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.
(42) Tsang, W. *Int. J. Chem. Kinet.* **1978**, *10*, 821.
(43) Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 1320. The data reported in this work were free energies at 600 K. Rotational symmetry numbers were taken into account to calculate the corresponding enthalpies at 300 K, which are used in the present discussion. (See ref 48.)
(44) Abboud, J.-L. M.; Hehre, W. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 6072.
(45) Jackson, J. A.; Lias, S. G.; Ausloos, P. *J. Am. Chem. Soc.* **1977**, *99*, 7515.
(46) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds", Academic Press: New York, 1970.
(47) Rossi, M.; Golden, D. M. Submitted for publication.
(48) Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417.
(49) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1978**, *100*, 1953.
(50) Ceyer, S. T.; Tiedemann, P. W.; Mahan, B. H.; Lee, Y. T. *J. Chem. Phys.* **1979**, *70*, 14.
(51) Houle, F. A.; Harding, L. B, submitted for publication in *Proc. Natl. Acad. Sci. U.S.A.* Briefly, the conclusions are as follows. Theoretical calculations[10,11,18] indicate that, in the absence of reorientation of methyl groups, the out-of-plane bending potentials of alkyl-substituted radicals are highly asymmetric and involve a single minimum. It is suggested that the origin of this effect lies in the orthogonality-induced bond-pair repulsions analogous to those leading to hindered internal rotations in alkanes. This interaction leads to an intimate coupling between the out-of-plane angle of the radical center and the torsional angle of the substituent methyl groups. Coupling of the torsional and out-of-plane modes leads to potential surfaces with multiple minima separated by low barriers, such that the radicals appear to have free internal rotation.
(52) Vorachek, J. H.; Meisels, G. G.; Geanangel, R. A.; Emmel, R. H. *J. Am. Chem. Soc.* **1973**, *95*, 4078.
(53) Ausloos, P.; Lias, S. *J. Chem. Phys.* **1962**, *36*, 3163.
(54) Ausloos, P.; Rebbert, R. E.; Sieck, L. W.; Tiernan, T. O. *J. Am. Chem. Soc.* **1972**, *94*, 8939. A previous ICR study by Jaffe, H. H.; Billets, S. *J. Am. Chem. Soc.* **1972**, *94*, 674, which indicated that unrearranged ethyl cations were formed at threshold, was refuted by this work.
(55) (a) Saunders, M; Hagen, E. L. *J. Am. Chem. Soc.* **1970**, *90*, 6881. (b) Radom, L.; Pople, J. A.; Buss, V.; von R. Schleyer, P. *ibid.* **1972**, *94*, 311.
(56) Although H-scrambling rates in *tert*-butyl cation have not been measured, the process would involve a primary cation, and therefore have a high activation energy. Furthermore, its IR spectrum is consistent with a species having C_3 symmetry.[25]
(57) Rabalais, J. W. "Principles of Ultraviolet Photoelectron Spectroscopy", Wiley-Interscience: New York, 1977.
(58) Although the stated uncertainties in the data are ±0.02 eV, the reproducibility of the measured IPs is much higher. The reported adiabatic IPs are taken from the following raw data, obtained with Ne I radiation: CH_3CH_2 (8.391, 8.395) and CH_3CD_2 (8.380, 8.380, 8.382). Similarly, the He I and Ne I vertical IPs are: CH_3CH_2 (8.511, 8.509, 8.511, 8.510) and CH_3CD_2 (8.501, 8.500, 8.500, 8.507, 8.505). Thus, the 0.01-eV lowering of the IP of ethyl radical on deuteration is significant.
(59) Houle, F. A.; Beauchamp, J. L.; Prakash, G.; Olah, G. A. *J. Am. Chem. Soc.* To be submitted.
(60) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* To be submitted.
(61) Koenig, T.; Chang, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 2240.
(62) Baghal-Vayjooee, M. H.; Colussi, A. J.; Benson, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 3214.
(63) Tsang, W. *J. Phys. Chem.* **1972**, *76*, 143.
(64) Marshall, R. M.; Purnell, H.; Storey, P. D. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 85.
(65) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1* **1977**, *6*.
(66) JANAF Thermochemical Tables. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1971**, *No. 37*.

A Photoelectron Spectroscopic–Molecular Orbital Study of SF_4 and Related Fluorosulfuranes

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Abstract: He(I) photoelectron spectra (UPS) are reported for SF_4, CF_3SF_3, $(CF_3)_2SF_2$, Me_2NSF_3, $(Me_2N)_2SF_2$, $F_3SCF_2SF_3$, and $(CF_3)_2S$. The UPS of SF_4 was interpreted on the basis of SCF-X_α scattered-wave (X_α SW) calculations in which the ionization energies (IEs) of all the valence molecular orbitals (MOs) were computed by the transition-state method. MNDO MO calculations have also been performed on SF_4. The observation that the F(2p) π-type orbitals are ~2 eV more stable in the equatorial than in the axial sites is consistent with a previous X-ray photoelectron spectroscopic study of SF_4. The UPS of the other fluorosulfuranes were interpreted using qualitative arguments and on the basis of empirical trends in the IEs. For all the fluorosulfuranes studied here a correlation was noted between the IE of the sulfur "lone-pair" MO and the sum of the group electronegativities of the equatorial substituents. A detailed discussion of the $7a_1$, $3b_1$, $4a_1$, $2b_2$, $2b_1$, and $3a_1$ MOs of SF_4 is presented from the standpoint of the X_α SW calculations. The HOMO ($7a_1$) involves approximately equal charge densities on the sulfur atom and each of the axial fluorine (F_a) ligands. The $3b_1$ MO features a modicum of bonding interaction between the axial and equatorial fluorine ligands. The orbital contour map for the $2b_1$ MO is reminiscent of the hypervalent three-center, four-electron model for F_a-S-F_a bonding.

I. Introduction

The sulfuranes are well-known examples of chemical systems in which the classical Lewis octet of the central atom is expanded. Dubbed "hypervalent" by Musher,[1] molecules of this general type have attracted the attention of both theoretical and structural chemists. From a practical standpoint, fluorosulfuranes play an important role as fluorinating agents[2] and as precursors for the synthesis of sulfonium cations.[3]

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The simplest known sulfurane is SF_4; its structure is usually described as trigonal bipyramidal,[4] one of the equatorial sites being occupied by a sulfur lone pair (Figure 1). Other sulfuranes have been found to possess comparable skeletal geometries.[5]

From a qualitative standpoint, the electronic structure of, e.g., SF_4 can be discussed in terms of sp^3d hybridization at the sulfur atom, or by means of a model which avoids S(3d) orbital participation by invoking a three-center, four-electron description for the axial bonds.[1,6] In the wake of computational advances many molecular orbital (MO) calculations of varying degrees of sophistication have been carried out on SF_4[7] and the model sulfurane, SH_4.[8]

The basic motivation of the present work was to measure the UV photoelectron spectra (UPS) of SF_4, the related sulfuranes CF_3SF_3, $(CF_3)_2SF_2$, Me_2NSF_3, and $(Me_2N)_2SF_2$, and the bissulfurane $F_3SCF_2SF_3$ in order to provide experimental ionization energy (IE) data pertinent to a discussion of the bonding in molecules of this type. Previous photoelectron spectroscopic work on the sulfuranes is confined to one X-ray photoelectron spectroscopic (XPS) study[9] of SF_4.

SCF X_α scattered-wave calculations[10] (hereafter referred to as X_α SW) have been performed on SF_4 to facilitate the UPS interpretations. As is well-known, the X_α SW method circumvents the use of Koopmans' theorem[11] by direct calculation of IEs by means of the transition-state method.[12] One X_α SW calculation has, in fact, been performed on SF_4 already.[7a] However, we opted to perform such calculations locally because in the previous work transition-state calculations were reported only for the ionization of MOs of a_1 symmetry. Furthermore, we wished to explore the sensitivity of the results to the choice of atomic sphere radii. Our X_α SW results are in essential agreement with those of Rösch, Smith, and Whangbo;[7a] however, we present a somewhat more detailed discussion of the electronic structure of SF_4.

II. Experimental Section

Materials. Sulfur tetrafluoride was procured commercially and purified by reaction with BF_3 followed by the addition of dry Et_2O.[3b] The compounds CF_3SF_3,[13] $(CF_3)_2SF_2$,[14] Me_2NSF_3,[15] $(Me_2N)_2SF_2$,[2c] $F_3SCF_2SF_3$,[16] $(CF_3)_2S$,[17] and $CF_3S(O)F$[18] were prepared and purified as described in the literature.

Spectroscopic Measurements. All UPS were recorded on a Perkin-Elmer Model PS-18 spectrometer using a He(I) source (21.22 eV). The volatile sample inlet probe was used for all the compounds and each spectrum was calibrated with xenon (12.130 eV) and argon (15.759 eV) lines. All IEs are taken to be the band maxima unless noted otherwise. Spectral resolution was maintained between 20 and 50 meV for the argon line, except for the $(CF_3)_2SF_2$ and $(CF_3)_2S$ samples, when it degraded to ~100 meV. The liquid nitrogen trap on the spectrometer was kept full while the samples were introduced into the system. In the cases of SF_4 and CF_3SF_3, the samples were vaporized from quartz tubes containing NaF which acted as a scavenger for HF. Despite all precautions, the UPS of CF_3SF_3 could not be obtained free of traces of $CF_3S(O)F$. (The UPS of the latter does not appear to have been reported previously and it was therefore necessary to measure it in the present study.)

A copper-beryllium "venetian blind" multiplier tube was employed for the detection of the photoelectrons. Even though many of the compounds studied here are vigorous fluorinating agents, no significant degradation of the photomultiplier was apparent providing that the samples were very pure. However, if a sample containing trace impurities was run, a significant loss in the photomultiplier gain occurred. Interestingly, we found that baking the photomultiplier tube in a 350 °C oven under a slow stream of oxygen restored the device to a satisfactory level of performance.

Computational Procedures. The X_α SW calculations on SF_4 were made by employing the spin-restricted procedure of Johnson and Slater.[10] The requisite bond distances and angles for SF_4 were taken from the microwave study[4a] and are illustrated in Figure 1. The atomic sphere radii for the sulfur and fluorine atoms were chosen on the basis of optimizing the virial ratio.[19] The most satisfactory value ($-2T/V$ = 0.994) was obtained with tangential rather than overlapping spheres.[20] The outer sphere, centered at sulfur, was chosen tangential to the axial fluorine (F_a) sphere. Schwartz's exchange parameters,[21] α_{HF}, were used for all the atomic spheres, while the exchange parameter for the outer sphere was taken to be α_F. The intersphere exchange parameter, α_{INT}, was taken to be 0.735 05, on the basis of averaging the atomic α values according to the numbers of valence electrons. Spherical harmonics were employed through $l = 2$ for the sulfur and outer spheres, while functions through $l = 1$ were employed for the fluorine spheres. All SCF calculations were converged to better than 0.01 eV for each level, maintaining all cores fixed. All IEs for SF_4 were computed by the transition-state method.[10]

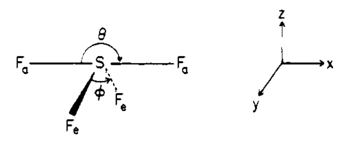

Figure 1. Structure of SF_4;[4a] $\theta = 186.93°$, $\phi = 101.55°$, $d_{SF_a} = 1.646$ Å, $d_{SF_e} = 1.545$ Å.

As a check on the reliability of the preceding calculation, other X_α SW computations were carried out both with and without an empty sphere to approximate the sulfur "lone pair". The principal effect of overlapping the spheres was to raise the energy of each level by a constant amount. Inclusion of an empty sphere had virtually no effect on the energy levels. Changing the atomic spheres to a 2:1 ratio of sulfur to fluorine did modify the spacings of the levels somewhat; however, the basic ordering was preserved. In view of the foregoing, only the results of the prior calculation are presented in detail.

MNDO calculations were performed as described in the literature.[22] These, and all other computations, were performed on the CDC 6400/6600 system at the University of Texas at Austin.

III. Results and Discussion

Interpretation of the UV Photoelectron Spectrum of SF_4. As pointed out in the Introduction, several molecular orbital calculations have been carried out on SF_4 and the model sulfurane, SH_4. A summary of the eigenvalues computed for SF_4 by various methods appears in Figure 2. Note that this compilation includes only occupied MOs and excludes the more tightly bound orbitals featuring significant F(2s) character. Furthermore, we have in some instances changed the naming of the MOs to conform to that employed in the X_α SW method. Of course, it is recognized that the X_α SW eigenvalues cannot be compared rigorously to those obtained by Hartree-Fock methods; nevertheless, it is often found that, from a purely empirical viewpoint, the X_α SW orbital orderings and Hartree-Fock eigenvalues are in good agreement with each other. Indeed, when the IEs of SF_4 are computed by the transition-state method (Table I) an identical ordering persists because all the ground-state orbitals (Table II) relax to approximately the same extent (ca. 4 eV).

One very conspicuous feature of Figure 2 is that, regardless of the computational method, the $7a_1$ level emerges as the highest occupied molecular orbital (HOMO), and is well separated from any of the remaining occupied MOs. The first ionization of SF_4, I_1 (Figure 3), can thus be assigned confidently to electron ejection from the $7a_1$ MO and the production of SF_4^+ in a $^2A_1$ electronic state. Some authors have referred to the $7a_1$ MO as the sulfur "lone pair"; however, this is not a simple matter and we defer a discussion of the composition of this and other MOs until later in the paper.

Following the HOMO is a set of four closely spaced levels, $2a_2$, $4b_1$, $6a_1$, and $4b_2$, which are, in essence, symmetry-adapted combinations of F(2p) C_{2v} nonbonding MOs localized on the axial fluorine (F_a) ligands. There is some discord between the CNDO/2 and other methods regarding the sequencing of these F_a "lone pair" MOs; however, we opt for the assignment of I_2 (Figure 3 and Table I) to electron ejection from the $2a_2$ and $4b_1$ MOs, and I_3 to ionization from the $6a_1$ and $4b_2$ MOs on

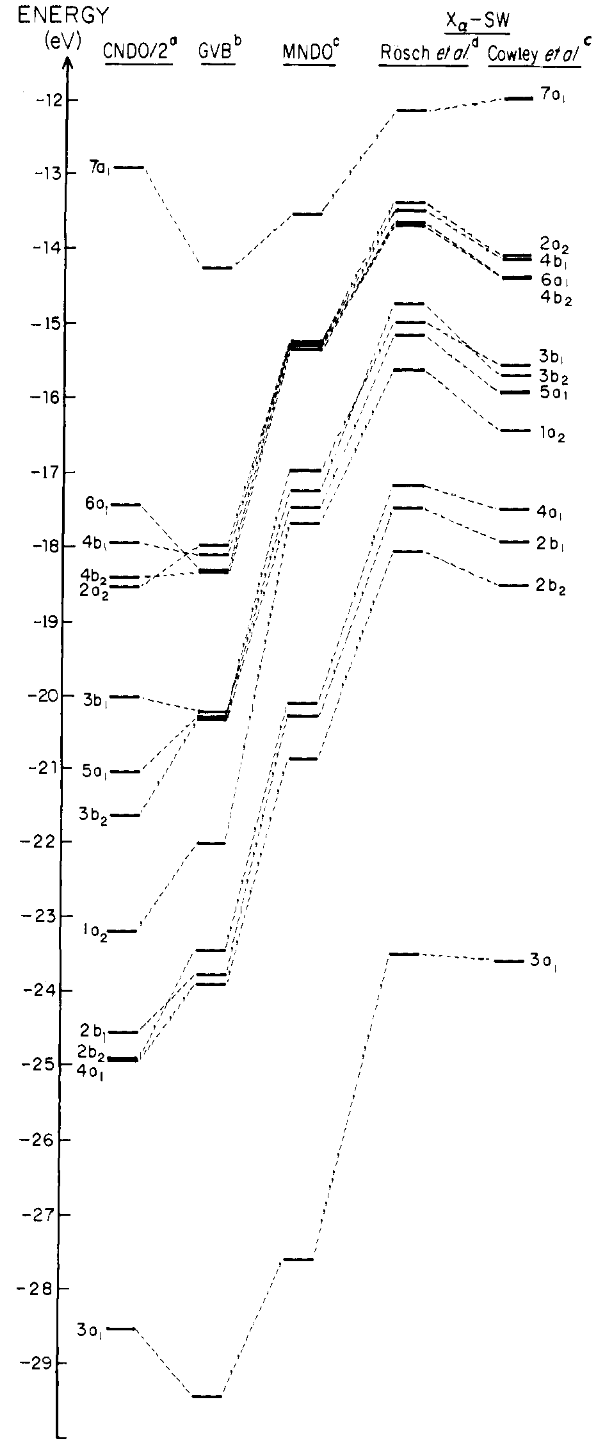

Figure 2. Eigenvalues computed for SF_4 by various methods using all valence electrons: (a) ref 7b, (b) ref 7d, (c) present work, (d) ref 7a.

the basis of the IEs computed for SF_4 by the transition-state method.

Following the F_a nonbonding MOs are the corresponding, predominantly F(2p) lone-pair combinations on the equatorial fluorine ligands (F_e) which span the irreducible representations $3b_1$, $3b_2$, $5a_1$, and $1a_2$. From the standpoint of the IEs computed by the X_α SW method, peaks I_4 and I_5 in the experimental spectrum are associated with the ionization from these MOs. It would be imprudent to be any more specific on these particular assignments because (a) the computed IEs are close in energy and (b) our X_α SW calculation differs from that of Rösch, Smith, and Whangbo[7a] regarding the ordering of the $3b_1$ and $3b_2$ levels. It is interesting to note that the UPS assignments for the F_a and F_e (2p) lone-pair combinations presented above are entirely consistent with the XPS result on SF_4.[9] The latter showed that the 1s electrons of the F_e ligands are 2.4 eV more tightly bound than the F_a ligands. In the UPS experiment the F(2p) orbitals are ca. 2.0 eV more tightly bound in the equatorial than the axial location.

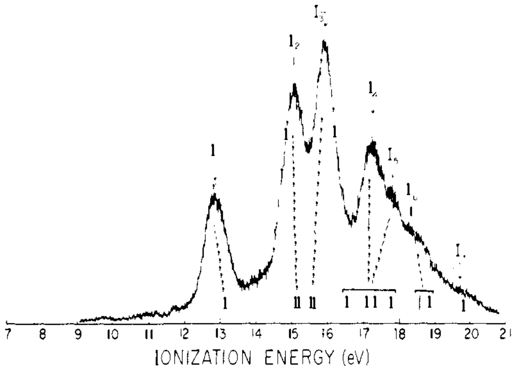

Figure 3. He(I) UPS of SF_4. The vertical bars represent the computed ionization energies uniformly shifted by ~3 eV to obtain a "best fit" with observed spectrum.

Table I. Theoretical and Experimental Ionization Energies for SF_4

MO	ionization energy computed by transition state method, eV	exptl ionization energy, eV
$7a_1$	16.06	12.85
$2a_2$	18.15	15.07
$4b_1$	18.17	
$6a_1$	18.52	15.8
$4b_2$	18.55	
$3b_1$	19.41	
$3b_2$	20.21	17.23
$5a_1$	20.00	17.7
$1a_2$	20.59	
$4a_1$	21.48	18.3
$2b_1$	21.77	
$2b_2$	22.73	19.5
$3a_1$	27.81	

As will be demonstrated later, the next three MOs, viz., $4a_1$, $2b_1$, and $2b_2$, account for much of S-F σ bonding in SF_4. Relying on the transition-state computed IEs (Table I), we are inclined to associate peak I_6 with electron ejection from the $4a_1$ and $2b_1$ MOs, and the barely discernible spectral feature, I_7, with ionization from the $2b_2$ MO. The latter assignment should, however, be viewed with caution because of the diminution of spectral intensity as the 21.22-eV limit of He(I) UPS is approached.

Overall comparison of the computed and experimental IEs in Table I and Figure 3 reveals that, while the computed values are too large by ~3 eV, the differences in energy predicted by the transition-state method are fairly satisfactory.

Finally, while not presenting a detailed discussion of our MNDO calculations on SF_4, it is clear from Figure 2 that within the framework of Koopmans' theorem[11] this method produces a reasonable description of the experimental spectrum. To achieve this result, however, it was necessary to restrain SF_4 to the experimental structural parameters, since geometry optimization afforded a tetrahedral configuration akin to that of, e.g., SiF_4!

Interpretation of the UV Photoelectron Spectra of Other Fluorosulfuranes. At the outset it should be pointed out that we have used the same system of MO numbering for the remaining fluorosulfuranes that was employed for SF_4. Ob-

Table II. X_α SW "Ground State" Eigenvalues and Charge Densities[a] for SF_4

MO	ϵ^b	S				F_e			F_a			OUTR[c]	INT[d]
		s	+ p	+ d	= total	s	+ p	= total	s	+ p	= total	total	total
$5b_1$	−2.50		0.36	0.01	0.37		0.01	0.01	0.02	0.11	0.13	0.07	0.28
$8a_1$	−4.50	0.14	0.13	0.00	0.27	0.01	0.08	0.09	0.00	0.03	0.03	0.09	0.40
$5b_2$	−5.92		0.31	0.05	0.36	0.01	0.06	0.07		0.02	0.02	0.02	0.44
$7a_1$	−12.02	0.10	0.11	0.02	0.23	0.00	0.02	0.02	0.00	0.24	0.24	0.01	0.24
$2a_2$	−14.15			0.00	0.00		0.08	0.08		0.32	0.32	0.00	0.20
$4b_1$	−14.20		0.00	0.00	0.00		0.10	0.10	0.00	0.31	0.31	0.00	0.18
$6a_1$	−14.41	0.00	0.00	0.01	0.01	0.00	0.04	0.04	0.00	0.36	0.36	0.01	0.18
$4b_2$	−14.43		0.00	0.00	0.00	0.00	0.03	0.03		0.36	0.36	0.01	0.21
$3b_1$	−15.57		0.04	0.00	0.04		0.16	0.16	0.00	0.21	0.21	0.02	0.20
$3b_2$	−15.75		0.00	0.00	0.00	0.00	0.38	0.38		0.00	0.00	0.00	0.24
$5a_1$	−15.93	0.01	0.03	0.02	0.06	0.00	0.28	0.28	0.00	0.08	0.08	0.01	0.21
$1a_2$	−16.44			0.01	0.01		0.30	0.30		0.07	0.07	0.01	0.24
$4a_1$	−17.50	0.02	0.11	0.01	0.14	0.00	0.22	0.22	0.00	0.05	0.05	0.01	0.31
$2b_1$	−17.94		0.12	0.00	0.12		0.12	0.12	0.01	0.18	0.19	0.00	0.26
$2b_2$	−18.52		0.14	0.01	0.15	0.01	0.28	0.29		0.02	0.02	0.01	0.22
$3a_1$	−23.53	0.39	0.00	0.00	0.39	0.03	0.09	0.12	0.03	0.04	0.07	0.00	0.23
$2a_1$	−33.36	0.01	0.00	0.01	0.02	0.05	0.00	0.05	0.37	0.00	0.37	0.01	0.13
$1b_1$	−33.50		0.02	0.00	0.02		0.00	0.00	0.42	0.00	0.42	0.01	0.13
$1b_2$	−35.42		0.02	0.01	0.03	0.40	0.00	0.40		0.00	0.00	0.00	0.17
$1a_1$	−36.43	0.07	0.01	0.00	0.08	0.32	0.00	0.32	0.04	0.00	0.04	0.00	0.20

[a] Charge densities for atoms are percentages of electron densities within the atomic spheres. [b] Eigenvalues in eV. [c] Charge density outside outer sphere. [d] Intersphere charge density inside outer sphere and not accounted for by atomic spheres. Dashed line denotes separation of HOMO and LUMO.

Table III. Experimental Ionization Energies (eV)[a] for Various Fluorosulfuranes and $(CF_3)_2S$

	I_1	I_2	I_3	I_4	other IEs
SF_4	12.85[b]	15.07	15.8	17.23	17.7, 18.3, 19.5
CF_3SF_3	12.4[b]	14.1	14.9	15.7	16.0, 17.3, 17.9, 19.0
$(CF_3)_2SF_2$	12.1[b]	13.4	14.0	14.9	16.0, 16.5, 17.0, 17.3, 17.7
Me_2NSF_3	9.92[c]	11.57[b]	13.3	13.7	14.3, 15.7, 16.4, 18.3
$(Me_2N)_2SF_2$	8.83[c]	9.52[c]	10.64[b]	12.4	13.0[d]
$F_3SCF_2SF_3$	12.1[b]	12.81[b]	13.6	14.8	15.5, 15.8, 17.3, 17.9, 19.1
$(CF_3)_2S$[e]	11.35	13.6	14.1	16.0	16.6, 17.38, 18.39

[a] Assignments indicated for only $7a_1$ MO and nitrogen lone-pair MOs. See text for further assignments. [b] Assigned to $7a_1$ MO. [c] Assigned to nitrogen lone-pair MOs. [d] Other ionizations not resolved. [e] I_1, I_2, and I_3 assigned to b_1, a_1, and b_2 MOs of R_2S, respectively (see text).

viously this is incorrect in a formal sense, but we believe that such a system is less confusing than changing the orbital labeling from compound to compound.

Attention is focused initially on the CF_3-substituted fluorosulfuranes, $(CF_3)_2SF_2$ and CF_3SF_3.[23] It is perhaps instructive to consider that $(CF_3)_2SF_2$ is derived by the addition of two fluorine ligands to the sulfide, $(CF_3)_2S$. The UPS of $(CF_3)_2S$ has, in fact, been recorded previously[24] but, unfortunately, only the adiabatic IEs were reported. Our He(I) UPS data for $(CF_3)_2S$ are presented in Table III. It is readily interpreted by analogy to the assignments for the methyl analogue, $(CH_3)_2S$.[25] Thus, I_1 corresponds to ionization from the b_1 HOMO which is essentially pure S(3p) in character, while peaks I_2 and I_3 are assigned to ionization from the S-C σ-bonding MOs of a_1 and b_2 symmetry, respectively.

By analogy with SF_4, the first peak in the UPS of $(CF_3)_2SF_2$ (Figure 4a) is assigned to ionization from the $7a_1$ MO. The only plausible assignments for peaks I_2 and I_3 are to attribute them to electron ejection from the S-C σ-bonding MOs of a_1 and b_2 symmetry, respectively, as in the case of $(CF_3)_2S$. On the basis of the closeness in energy of peak I_2 in SF_4 (15.07 eV) with peak I_4 in $(CF_3)_2SF_2$ (14.9 eV) we are inclined to assign the latter to the ionization from the $2a_2$ and $4b_1$ $F_a(2p)$ lone-pair combinations as we did in the case of SF_4. Definitive spectral assignments beyond 16 eV are precluded by the presence of ionizations from an appreciable number of C-F σ-bonding MOs.

It was impossible to obtain the UPS of CF_3SF_3 without the presence of trace quantities of $CF_3S(O)F$. The relatively low symmetry of CF_3SF_3 (C_s)[23] renders quantitative assignments difficult because extensive interactions among the various MOs of a′ and a″ symmetry become allowed. However, by analogy with the foregoing discussion of the UPS of $(CF_3)_2SF_2$ it is reasonable to attribute peak I_1 in the UPS of CF_3SF_3 (Figure 4b) to electron ejection from a HOMO of a′ symmetry akin to the $7a_1$ MO of SF_4. Arguing again by analogy with the UPS of $(CF_3)_2SF_2$, it is probable that peak I_2 in the UPS of CF_3SF_3 arises from the ionization of an S-C σ-bonding MO, and that I_3 corresponds to electron ejection from an MO comprising substantial $F_a(2p)$ lone-pair character.

We turn now to a discussion of the UPS of the Me_2N-substituted fluorosulfuranes. The presence of a single, low IE band (9.92 eV) in the UPS of Me_2NSF_3[26] (Figure 4c) which is well separated from any other band suggests very strongly that it is due to ionization from an MO which is of predominant N(2p) "lone-pair" character. This conclusion is in accord with a comparable assignment made for I_1 in the UPS of the phosphorane, Me_2NPF_4.[27] The trend in nitrogen lone-pair IEs, Me_2NPF_4 (10.35 eV) > Me_2NSF_3 (9.92 eV) > Me_3N (8.54 eV),[28] is expected on the basis of the group electronegativity sequence $-PF_4$ > $-SF_3$ > CH_3. The UPS of $(Me_2N)_2SF_2$ features two lower energy ionizations, I_1 and I_2 (Figure 4d). We have recently determined the structure of this compound by X-ray crystallography[5h] and found the molecule to possess a C_2 skeletal geometry with the two nitrogen atoms adopting a geometry approximately midway between trigonal planar

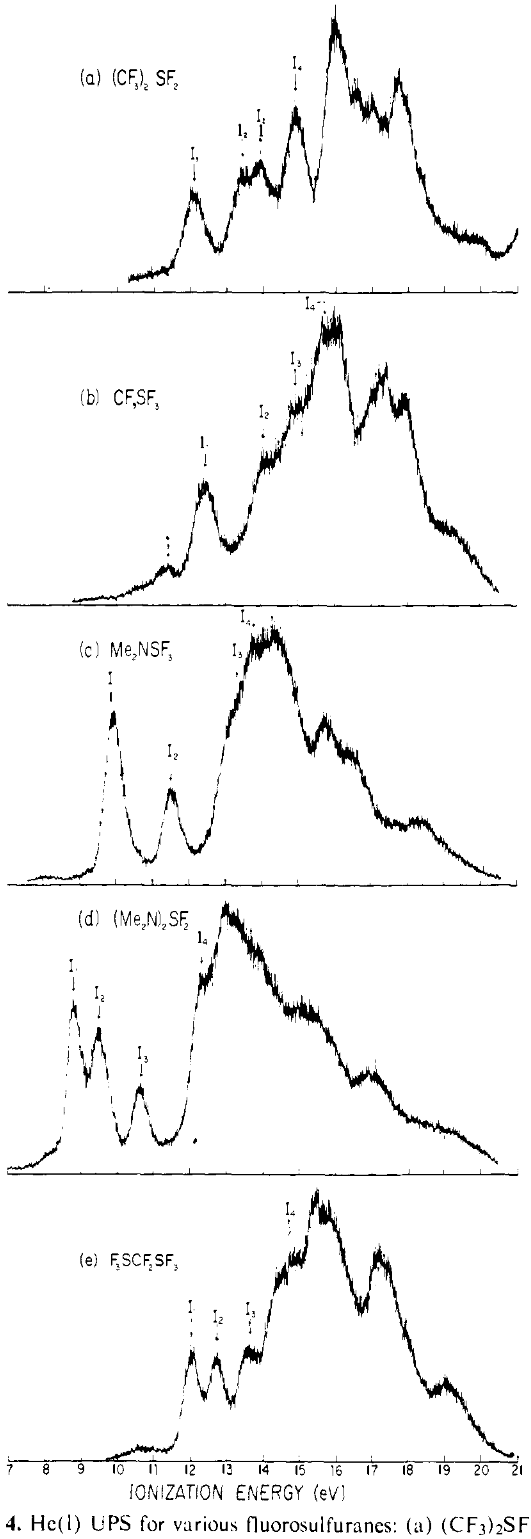

Figure 4. He(I) UPS for various fluorosulfuranes: (a) $(CF_3)_2SF_2$; (b) CF_3SF_3 (asterisk indicates peak due to $CF_3S(O)F$ impurity); (c) Me_2NSF_3; (d) $(Me_2N)_2SF_2$; (e) $F_3SCF_2SF_3$.

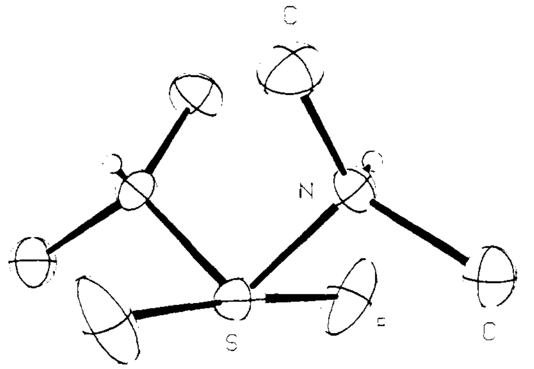

Figure 5. Structure of $(Me_2N)_2SF_2$.[5h] The thermal ellipsoids are drawn at the 30% probability level. The nitrogen lone pair directions are indicated by small blank spheres. The methyl hydrogens are omitted.

and tetrahedral. It is clear from Figure 5 that the two equivalent nitrogen lone-pair MOs could interact via a "through-bond" or "through-space" mechanism. The lone-pair splitting energy, ΔE, of 0.69 eV is less than that found in the corresponding phosphorane, $(Me_2N)_2PF_3$ (1.11 eV).[27] In view of the arguments presented above for SF_4 and the CF_3-substituted fluorosulfuranes we are inclined to assign peaks I_2 and I_3 in the UPS of Me_2NSF_3 and $(Me_2N)_2SF_2$, respectively, to ionization from the sulfur "lone-pair" MO, i.e., an orbital corresponding to the $7a_1$ MO in SF_4. The relative ordering $SF_4 > Me_2NSF_3 > (Me_2N)_2SF_2$ for this IE is expected on the basis of progressively replacing F_e by less electronegative Me_2N ligands.

Finally, we consider the UPS of the novel bissulfurane $F_3SCF_2SF_3$. On energetic grounds it seems reasonable to assign the first two peaks (Figure 4e) to sulfur "lone-pair" ionizations akin to that of the $7a_1$ MO of SF_4. Note that the average of these IEs, 12.45 eV, is very close to that of the monosulfurane, CF_3SF_3. By analogy with the UPS interpretations set forth above for $(CF_3)_2SF_2$ and CF_3SF_3 we assign peak I_3 in the spectrum of $F_3SCF_2SF_3$ to ionization from an S-C σ-bonding MO.

An interesting correlation was noted between the IE corresponding to electron ejection from the sulfur "lone pair" MO (the $7a_1$ MO in the case of SF_4) and the sum of the group electronegativities[29] of the equatorial substituents $\sum\chi_e$. The regression line shown in eq 1 is based on all the fluorosulfuranes studied here (except $F_3SCF_2SF_3$):

$$\mathrm{IE} = 0.73(\Sigma\chi_e) + 7.10 \qquad r^2 = 0.992 \qquad (1)$$

The fact that there is essentially no deviation from the regression line in the cases of Me_2NSF_3 and $(Me_2N)_2SF_2$ suggests that there is only minimal π-type interaction between the sulfur and nitrogen "lone pairs". This is consistent with the X-ray crystallographic result[5h] on $(Me_2N)_2SF_2$ which shows the dihedral angle between the sulfur and nitrogen lone pairs to be 120° with the major lobes pointing away from each other (Figure 5).

If the local geometry around each sulfur atom in $F_3SCF_2SF_3$ is assumed to be similar to that in CF_3SF_3,[23] and the electronegativity of the F_3SCF_2 moiety of $F_3SCF_2SF_3$ is approximated by that of the CF_3CF_2 substituent, a sulfur "lone-pair" IE of 12.43 eV would be computed according to eq 1. The average of the first two IEs of $F_3SCF_2SF_3$ is, in fact, 12.45 eV. The close correspondence of these numbers thus suggests that the first two peaks in the UPS of $F_3SCF_2SF_3$ arise from the interaction of equivalent sulfur "lone pairs" rather than from two sulfur "lone pairs" in different stereochemical environments. Structural information on $F_3SCF_2SF_3$ will clearly be of interest on this point.

The Molecular Orbitals of SF_4. Much of the discussion of the electronic structure of SF_4 has been concerned with the nature of the HOMO. This is a matter of considerable importance since, in principle, one might expect that SF_4 could behave as a ligand in a somewhat similar manner to PF_3. There is, in fact, only one instance of the ligative behavior of SF_4 and this is toward an oxygen atom in the compound $F_4S(O)$.[30] The CNDO/2[7b] and the present MNDO calculations place most of the electron density of the HOMO in the $2p_x$ orbitals of the F_a ligands. On the other hand, the VESCF[7e] and GVB[7f]

Table IV. Atomic Populations and Charge Distributions for SF_4

	atomic sphere populations					
	s	p	d	INT[a]	OUTR[b]	net atomic charges
S	1.20	1.19	0.20	6.97	0.26	S: +2.18
F_e	1.63	4.21				F_e: −0.34
F_a	1.75	4.50				F_a: −0.75

[a] Intersphere charge distributed to sulfur (6/32 × INT) and each fluorine (7/32 × INT). [b] Outer sphere charge distributed equally among the fluorines.

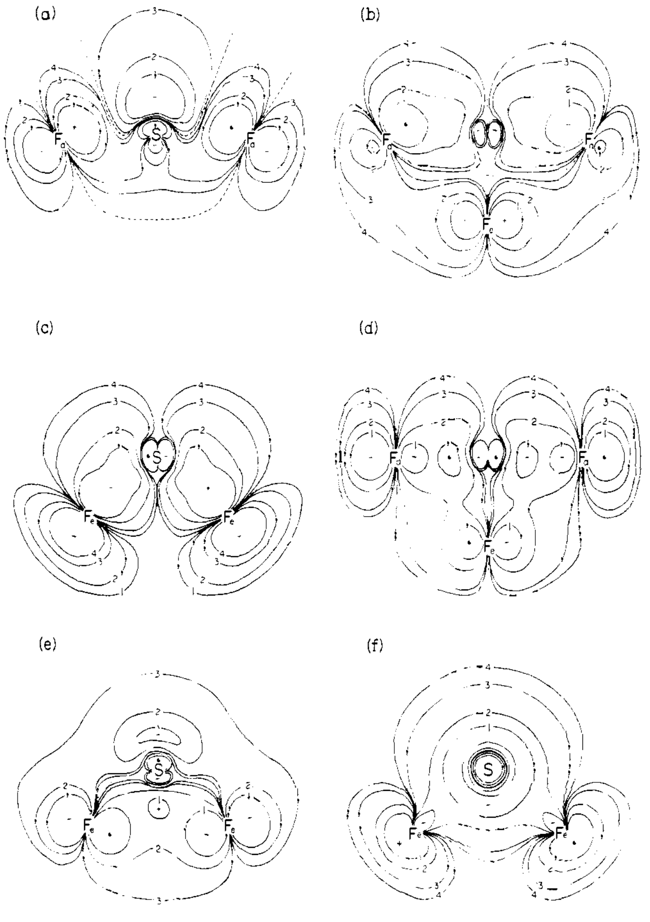

Figure 6. X_α SW contour plots for some MOs of SF_4: (a) $7a_1$ (xz plane); (b) $3b_1$ ($F_aF_eF_a$ plane); (c) $2b_2$ (yz plane); (d) $2b_1$ ($F_aF_eF_a$ plane); (e) $4a_1$ (yz plane); (f) $3a_1$ (yz plane). Contour values: 1 = ±0.13; 2 = ±0.07; 3 = ±0.02; 4 = ±0.01. Dashed lines are nodal planes.

methods show that the HOMO involves considerable admixture of the F_a contributions with sulfur orbitals of $3p_z$ and 3s character. Both the present X_α SW calculation and that reported earlier by Rösch, Smith, and Whangbo[7a] place approximately equal charge densities on the sulfur atom and each of the axial fluorine ligands. The contour plot (Figure 6a) of the $7a_1$ MO of SF_4 in the xz plane clearly illustrates this point.

An alternative way of looking at the HOMO of SF_4 is to consider that this molecule is the product of oxidative addition of two fluorine atoms to SF_2 (Figure 7). Note that, in order to arrive at the X_α SW description of the HOMO, it is necessary for the a_1 combination of F_2 p-σ orbitals to interact with an MO of a_1 symmetry of SF_2. Perhaps the interaction involves the unoccupied antibonding a_1 MO as well as the occupied bonding a_1 MO of SF_2 as indicated in Figure 7. This serves to cancel the density on the equatorial ligands in the resulting $7a_1$ MO of SF_4 (Table II).[7c] Similar analyses have, in fact, been presented for the hypothetical molecules SH_4[7c] and SF_2H_2.[8a] The slight tilting of the F_a $2p_x$ orbitals in the $7a_1$ MO of SF_4 (Figure 6a) may result from admixture of this orbital with the a_1 combination of F_a ($2p_z$) lone-pair orbitals (the $6a_1$ MO in Table II).[31]

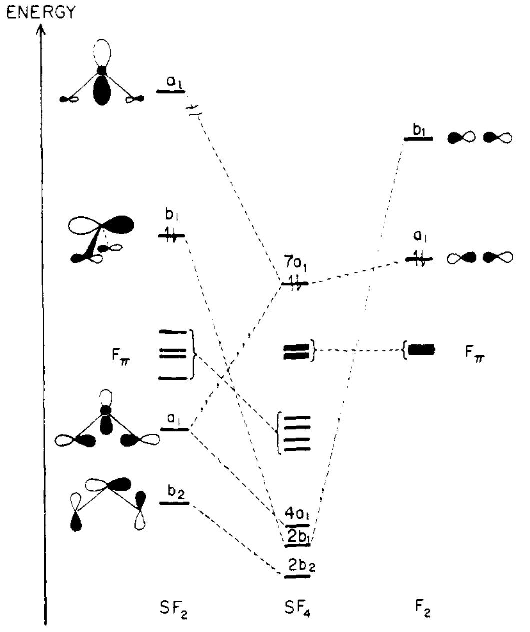

Figure 7. Correlation diagram for SF_4 based on MNDO calculations. The SF_2 calculation was based on the experimental[4a] F_e-S-F_e geometry of SF_4. The F_2 calculation was performed at the experimental[4a] F_a-S-F_a bond distance of SF_4. See text for details of the SF_4 calculation. The HOMO in each case is illustrated by ↑↓.

It was pointed out in the section dealing with the UPS assignments, and is also evident from the X_α SW charge densities (Table II), that the $2a_1$, $4b_1$, $6a_1$ and $4b_2$ MOs are essentially localized on the F_a(2p) lone-pair orbitals. Particular interest is associated with the nature of the $3b_1$ MO since, on qualitative group theoretical grounds, one expects this orbital to be a symmetry-adapted combination of F_e(2p) lone pairs. However, it is evident from Table II and also from the contour plot in Figure 6b that the $3b_1$ MO features bonding between the axial and equatorial fluorine ligands, in addition to some S-F_a bonding character.

The $2b_2$ and $4a_1$ MOs account for much of the σ bonding between the sulfur atom and the equatorial fluorine ligands. The contours for these MOs are displayed in Figures 6c and 6e, respectively. From the standpoint of the SF_4 correlation diagram (Figure 7) the $2b_2$ and $4a_1$ MOs can be considered to arise from the b_2 and a_1 σ-bonding orbitals. Likewise, the $2b_1$ MO of SF_4 can be considered to have as its origin the HOMO of SF_2; great stabilization occurring as σ bonding to the axial fluorine ligands becomes significant. This view is perhaps oversimplified, however, because, like the $3b_1$ MO, the $2b_1$ also features a bonding contribution from both the axial and equatorial fluorine ligands. The contour plot in Figure 6d shows that, as far as the F_a-S-F_a moiety is concerned, the bonding picture is not unlike that in the three-center four-electron bonding model.[1,6]

It is clearly apparent from Table II and Figure 6f that the $3a_1$ MO involves a large amount of S(3s) character and is extensively localized on the sulfur atom. However, the $3a_1$ MO also contributes to the σ bonding of SF_4, the emphasis being somewhat more on the S–F_e than the S–F_a bonds.

The final four valence MOs of SF_4 ($2a_1$, $1b_1$, $1b_2$, and $1a_1$) consist largely of F(2s) character and are essentially localized on the F_a and F_e ligands.

The atomic populations and charge distributions for SF_4 are presented in Table IV. The large positive charge on sulfur stems in part from the high electronegativity of the fluorine ligands. However, the magnitude of this charge is probably unrealistically large on account of the poor description of the sulfur "lone pair" in the X_α SW method.[10c] The accumulation of more charge on the F_a than the F_e ligands is also quite evident in Table IV and is a feature of all the MO calculations in SF_4 where such data are reported.[7]

Finally, we note that the correlation diagram shown in Figure 7 provides some insights into the reason for the feeble Lewis basicity of SF_4. In sulfides, R_2S, the HOMO of b_1 symmetry is predominantly of S(3p) character, and is responsible for the ligative behavior of these compounds.[32] In SF_4 the b_1 MO is involved in F_a–S–F_a bonding, leaving the somewhat diffuse $7a_1$ orbital as the HOMO.

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References and Notes

(1) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).

(2) (a) W. C. Smith, *Angew. Chem., Int. Ed. Engl.*, **1**, 467 (1962); (b) L. N. Markowski, V. E. Pashinnik, and A. V. Kiranov, *Synthesis*, 787 (1973); (c) W. J. Middleton, *J. Org. Chem.*, **40**, 574 (1975); (d) L. N. Markovski and V. E. Pashinnik, *Synthesis*, 801 (1975).

(3) (a) N. Bartlett and P. J. Robinson, *Chem. Ind. (London)*, 1351 (1956); (b) N. Bartlett and P. L. Robinson, *J. Chem. Soc.*, 3417 (1961); (c) F. Seel and O. Detmer, *Angew. Chem.*, **70**, 163 (1958); (d) F. Seel and O. Detmer, *Z. Anorg. Allg. Chem.*, **301**, 113 (1959); (e) A. H. Cowley, D. J. Pagel, and M. L. Walker, *J. Am. Chem. Soc.*, **100**, 7065 (1978).

(4) (a) M. W. Tolles and W. D. Gwinn, *J. Chem. Phys.*, **36**, 1119 (1962); (b) K. Kimura and S. H. Bauer, *ibid.*, **39**, 3172 (1963); (c) V. C. Ewing and L. E. Sutton, *Trans. Faraday Soc.*, **59**, 1241 (1963). We used the microwave data[4a] rather than the electron diffraction data[4b,c] in all our computations.

(5) (a) J. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971); A. Kálmán, K. Sasvári, and I. Kapovits, *Acta Crystallogr., Sect. B*, **29**, 355 (1971); (b) I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Am. Chem. Soc.*, **93**, 6674 (1971), **94**, 5010 (1972); (c) N. C. Baenzinger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *ibid.*, **91**, 5749 (1969); (d) E. F. Perozzi, J. C. Martin, and I. C. Paul, *ibid.*, **96**, 6735 (1974); (e) L. J. Adzima, E. N. Duesler, and J. C. Martin, *J. Org. Chem.*, **42**, 4001 (1977); (f) K. C. Hodges, D. Schomburg, J.-V. Weiss, and R. Schmutzler, *J. Am. Chem. Soc.*, **99**, 6096 (1977); (g) L. J. Adzima, C. C. Chiang, I. C. Paul, and J. C. Martin, *ibid.*, **100**, 953 (1978); (h) A. H. Cowley, J. S. Szobota, and M. L. Walker, submitted for publication.

(6) R. E. Rundle, *Surv. Prog. Chem.*, **1**, 81 (1963).

(7) (a) N. Rösch, V. H. Smith, and M.-H. Whangbo, *Inorg. Chem.*, **15**, 1768 (1976); (b) V. B. Koutecky and J. I. Musher, *Theor. Chim. Acta*, **33**, 227 (1974); (c) M. M. L. Chen and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1647 (1976); (d) P. J. Hay, *ibid.*, **99**, 1003 (1977); (e) R. D. Brown and J. B. Peel, *Aust. J. Chem.*, **21**, 2605, 2617 (1968); (f) L. Radom and H. F. Schaeffer III, *ibid.*, **28**, 2069 (1975).

(8) (a) R. Gleiter and A. Veillard, *Chem. Phys. Lett.*, **37**, 33 (1976); (b) G. M. Schwenzer and H. F. Schaeffer III, *J. Am. Chem. Soc.*, **97**, 1393 (1975).

(9) (a) R. W. Shaw, Jr., T. X. Carroll, and T. D. Thomas, *J. Am. Chem. Soc.*, **95**, 5870 (1973).

(10) (a) J. C. Slater, *Adv. Quantum Chem.*, **6**, 1 (1972); (b) K. H. Johnson, *ibid.*, **7**, 143 (1973); (c) *Annu. Rev. Phys. Chem.*, **26**, 39 (1975).

(11) T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).

(12) (a) J. C. Slater and K. H. Johnson, *Phys. Rev. B*, **5**, 844 (1972); (b) J. C. Slater, "Quantum Theory of Molecules and Solids" Vol. 4, McGraw-Hill, New York, 1974, p 583.

(13) R. W. Braun, A. H. Cowley, M. C. Cushner, and R. J. Lagow, *Inorg. Chem.*, **17**, 1679 (1978), and references cited therein.

(14) G. H. Sprenger and A. H. Cowley, *J. Fluorine Chem.*, **7**, 333 (1976), and references cited therein.

(15) G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, **6**, 1903 (1967).

(16) L. A. Shimp and R. J. Lagow, *Inorg. Chem.*, **16**, 2974 (1977).

(17) E. W. Lawless and L. D. Harman, *J. Inorg. Nucl. Chem.*, **31**, 1541 (1969).

(18) C. T. Ratcliffe and J. M. Shreeve, *J. Am. Chem. Soc.*, **90**, 5403 (1968).

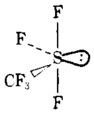
(19) (a) J. G. Norman, *J. Chem. Phys.*, **61**, 4630 (1974); (b) *Mol. Phys.*, **31**, 1191 (1976).

(20) $r_{OUTR} = 4.632$; $r_s = 1.588$; $r_{F_a} = 1.522$; $r_{F_e} = 1.332$ au.

(21) K. Schwartz, *Phys. Rev. B*, **5**, 2466 (1972).

(22) M. J. S. Dewar, M. McKee, and H. Rzepa, *J. Am. Chem. Soc.*, **100**, 3607 (1978), and references cited therein.

(23) The C_s structure i is based on NMR evidence. See R. W. Braun, A. H. Cowley, M. C. Cushner, and R. J. Lagow, *Inorg. Chem.*, **17**, 1679 (1978). By analogy, we anticipate that in $(CF_3)_2SF_2$ both CF_3 groups are located equatorially.



i

(24) W. R. Cullen, D. C. Frost, and D. A. Vroom, *Inorg. Chem.*, **8**, 1803 (1969).

(25) H. Bock and B. Solouki, *Chem. Ber.*, **107**, 2299 (1974).

(26) We presume that the Me_2N group of Me_2NSF_3 is located on an equatorial site of a trigonal bipyramidal sulfurane structure since both Me_2N groups of $(Me_2N)_2SF_2$ are arranged in this manner.[5h]

(27) A. H. Cowley, M. J. S. Dewar, D. W. Goodman, and J. R. Schweiger, *J. Am. Chem. Soc.*, **95**, 6506 (1973).

(28) (a) S. Cradock, E. A. V. Ebsworth, W. J. Savage, and R. A. Whiteford, *J. Chem. Soc. Faraday Trans. 2*, **68**, 934 (1972); (b) S. Elbel, H. Bergmann, and W. Ensslin, *ibid.*, **70**, 555 (1974).

(29) (a) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965); (b) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(30) (a) W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 3838 (1960); (b) H. Jonas, *Z. Anorg. Allg. Chem.*, **266**, 273 (1951); (c) F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78**, 290 (1956).

(31) We are indebted to a referee for suggesting this interaction.

(32) M. A. Weiner and M. Lattman, *Inorg. Chem.*, **17**, 1084 (1978).