tems is in the range 3-5. Thus we expect the observed activation energies to be approximately 3-5 kcal/mol less than the endothermicities of the dissociation reactions, and this is in agreement with our measured values.

A decrease in the activation energy of thermal unimolecular reactions at the low-pressure limit is predicted by the RRK theory as:[11]

$$E_a^0 = E_a^\infty - (s - 1)RT \qquad (9)$$

where E_a^0 and E_a^∞ are the activation energy at the low- and high-pressure limits, correspondingly, and s is the number of active oscillators in the sense of the Kassel theory. The absence of an activation energy for the association process indicates that the energy barriers for the dissociation are equal to ΔH; therefore $E_a^\infty \approx \Delta H_{\mathrm{dissoc}}$. Making reasonable guesses for the magnitudes of s ($s \approx \frac{1}{2}(3N - 6)$) one calculates from eq 9 that E_a^0 will again be less than E_a^∞ by several kilocalories per mole. It is also of interest to note that eq 8 and 9 yield the result that $n = s - 1$.

(5) Kinetics of the Thermal Decomposition of Cluster Ions. Preexponential Factors. Inspection of the preexponential factors for k_{-1} in Table III reveals that some of these values are larger by up to seven orders of magnitude than the collision rate between $AH^+ \cdot A$ and (M) which corresponds to $\log A \approx -9$, for A in units of $cm^3/(mol\ s)$. Preexponential factors higher by up to two orders of magnitude than the rate for activating collisions are common in decomposition reactions of neutral molecules. The effect is often attributed to activation involving internal degrees of freedom. In recent work on $H_3^+ \cdot H_2$ Hiraoka and Kebarle[12] found a preexponential factor of $\log A = -5.1$, which is four orders of magnitude larger than the collision rate between $H_3^+ \cdot H_2$ and H_2. We find preexponential factors for the decomposition of cluster ions which are larger by five to nine orders of magnitude than the calculated rate of activating collision, i.e., of $k_{\mathrm{collision}} e^{-E_a/RT}$, even when the already low activation energies given in Table III are used. It appears that unusually large preexponential factors are common in the thermal decomposition of gaseous ions, and we can offer no explanation for this interesting phenomenon.

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Generalized Valence Bond Studies of the Electronic Structure of SF_2, SF_4, and SF_6

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Abstract: The electronic structure of SF_2, SF_4, and SF_6 is investigated from the standpoint of ab initio generalized valence bond (GVB) calculations. Analysis of the GVB orbitals in these molecules and in the model reaction $SF_4 \rightarrow SF_2 + 2F$ leads to the conclusion that the stability of the hypervalent SF_4 and SF_6 systems is largely due to the incorporation of charge-transfer configurations, with 3d functions on the sulfur playing a lesser role. Molecular properties for SF_2 and SF_4 are reported.

The ability of elements in groups 5-8 to form more bonds than the classical octet rule permits has provided an intriguing topic in the modern development of the theory of electronic structure. The discovery of the xenon fluorides[1] in 1962 stimulated further activity in the area of "hypervalent" molecules.

In valence bond (VB) theory[2] the concept of the "expanded valence shell" was introduced whereby atoms could make use of d orbitals to form additional bonds. This notion has led to controversy over whether the promotion energies and spatial extent of d orbitals are consistent with the observed molecular properties.[3-6] The importance of ionic "resonance structures" has also been acknowledged in VB treatments.[2]

Molecular orbital (MO) theory provides a conceptual framework to treat nonclassical multicenter bonds without resorting to the expanded valence shell. After the discovery of the xenon fluorides it was demonstrated how MO treatments could describe these systems using s and p orbitals.[7-9]

Although examination of MO's can be particularly valuable in understanding charge distributions and geometrical preferences of molecules, the problem of determining chemical stability depends on evaluation of the matrix elements of the total energy of a molecule. Calculations at the Hartree-Fock level can lead to poor predictions of molecular binding energies when the two species have different numbers of bonds.[10]

Simpler schemes have been proposed by Coulson[11] and Pitzer[12] to explain the stability of hypervalent molecules which focus on the incorporation of charge-transfer configurations in the wave function.

In this paper we examine the electronic structure of SF_2, SF_4, and SF_6 using ab initio generalized valence bond (GVB) wave functions.[13,14] The GVB method can be viewed as a synthesis of valence bond (VB) and molecular orbital (MO) theories. It retains the VB form of the wave function but can still be analyzed in terms of a multiconfiguration wave function, where the configurations are comprised of (localized) molecular orbitals.

The GVB wave function is particularly well-suited for investigating this topic since the resulting localized orbitals can be analyzed in terms of d orbital participation and ionic character. It does not suffer from the drawbacks of either the VB formulation, which often imposes specific hybridization requirements on the orbitals, or the MO formulation, which tends to overemphasize the importance of ionic terms in the wave function.

GVB calculations have been reported for a number of first-row compounds, including ground states as well as excited states.[14,15] The present study is the first extension to "hypervalent" [16] compounds of second-row elements. Previous MO studies of sulfur fluorides have included extended Hückel,[17] CNDO,[18-20] and approximate nonempirical treatments.[21,22] Xα-scattered wave calculations have been reported for group 6 hexafluorides.[23,24] Ab initio treatments have included SF_6,[25,26] SF_2H_2,[27] and the hypothetical hydride analogues SH_4 and SH_6.[28]

Generalized Valence Bond Method

In the molecular orbital Hartree–Fock wave function for a closed shell molecule

$$a\ \phi_1\bar{\phi}_1\phi_2\bar{\phi}_2 \ldots \phi_n\bar{\phi}_n$$

each pair of electrons is described by a doubly occupied spatial orbital ϕ_i (a is the antisymmetrizer and ϕ_i and $\bar{\phi}_i$ have the usual meaning of spatial orbitals with associated α or β spin, respectively). The GVB wave function[13] replaces a pair $\phi_i(1)\bar{\phi}_i(2)$ by a valence bond form

$$\phi_{ia}(1)\bar{\phi}_{ib}(2) + \phi_{ib}(1)\bar{\phi}_{ia}(2)$$

where

$$\langle \phi_{ia} | \phi_{ib} \rangle \neq 0$$

The total wave function is formed by constructing products of such pairs. In the strong orthogonality approximation, the GVB orbitals of one pair (ϕ_{1a},ϕ_{1b}) are constrained to be orthogonal to the orbitals of all other pairs. Usually we shall take the bonding orbitals to have the GVB form while we keep the core orbitals and nonbonding orbitals doubly occupied as in MO theory. Open shell orbitals are similarly unaffected in a GVB wave function.

The orbitals in the GVB wave function are then optimized by varying the total energy subject to the above conditions. The GVB orbitals are therefore free to hybridize and delocalize to obtain the optimum form of the wave function. This is in contrast to usual VB formulations where arbitrary hybridizations and charge distributions are assumed.

The link between GVB orbitals and traditional MO theory is most apparent in the *natural orbital* (NO) form of the wave function. The above GVB form for pair i can be rewritten

$$\begin{aligned} &\phi_{ia}(1)\bar{\phi}_{ib}(2) + \phi_{ib}(1)\bar{\phi}_{ia}(2) \\ &\qquad = C_{i1}\phi_{i1}(1)\bar{\phi}_{i1}(2) - C_{i2}\phi_{i2}(1)\bar{\phi}_{i2}(2) \end{aligned} \quad (1)$$

where

$$C_{i2}{}^2 + C_{i2}{}^2 = 1$$

$$\langle \phi_{i1} | \phi_{i2} \rangle = 0$$

and $[\phi_{i1}, \phi_{i2}]$ are the natural orbitals for the pair. In this form the GVB wave function is seen to be a two-configuration representation in terms of doubly occupied orthogonal orbitals. If n pairs are so represented as a product of two-configuration NO pairs, the GVB wave function contains 2^n configurations.

If one sets $C_{i1} = 1$ and $C_{i2} = 0$ in each pair, one obtains the single-configuration Hartree-Fock function. The primary NO ϕ_{i1} (in general $C_{i1} \gg C_{i2}$ near the equilibrium geometry) differs from the molecular orbital ϕ_i in that the GVB natural orbital is usually localized in one of the bonding regions of the molecule, while the molecular orbital is delocalized over the molecule and has the full symmetry of the molecule. The pair lowering energy $\Delta\epsilon_i$ refers to the lowering in energy obtained for each pair relative to Hartree-Fock by adopting the two-configuration form.

In practice the calculations are carried out in terms of the orthogonal NO's, where the orbitals and CI coefficients are obtained each iteration. The GVB orbitals themselves are recovered by the relations:

$$\begin{aligned} \phi_{ia}, \phi_{ib} &= N(\phi_{i1} \pm \lambda\phi_{i2}) \\ N &= (1 + \lambda^2)^{-1/2} \\ \lambda &= (C_{i2}/C_{i1})^{1/2} \end{aligned} \quad (2)$$

The following discussion will employ both the GVB form and the NO form in the analysis depending on which better serves the purpose. The GVB form, which provides the connection to VB theories, is best suited for analyzing orbital hybridization, while the NO form is most convenient for Mulliken population analyses of the charge distributions.

Details of the Calculation

Basis Set and Geometries. A (9s5p) Gaussian basis contracted to [3s2p] was used for the fluorine atom.[29] For sulfur an (11s7p) basis[30] was contracted to [4s3p]. In each case the core orbitals (1s for F; 1s, 2s, and 2p for S) were contracted to a single function leaving a "double ζ" representation of the valence orbitals. This was accomplished without any loss of accuracy or speed with the general contraction scheme of Raffenetti.[31] A single 3d orbital ($\zeta = 0.6$) was added on the sulfur atom, where the exponent was optimized from calculations on SF_2.

Experimental geometries (Figure 1) were taken for SF_2 ($R = 1.589$ Å, $\theta = 98.3°$),[32] SF_4 ($R_1 = 1.545$ Å, $R_2 = 1.646$ Å, $\theta_1 = 101.5°$, $\theta_2 = 187°$),[33] and SF_6 ($R = 1.564$ Å, octahedral bond angles).[34]

Population Analysis. A standard Mulliken population analysis[35] was carried out for the Hartree-Fock and GVB wave functions. For a GVB wave function, the population on a given center p_A (or given atomic symmetry of a center) is defined

$$p_A = 2 \sum_i n_i p_{iA}$$

where p_{iA} is the Mulliken population on A for the ith GVB natural orbital, n_i is the occupation number (the square of the coefficient C_i in (1)), and the sum is over all orthogonal natural orbitals. For HF wave functions of closed shell systems, all n_i's are unity.

Since in general the overall charge distributions from the population analysis of GVB wave functions differ very little (less than 10%) from the HF wave functions, we will present only the *total* populations from HF calculations.

The *contributions* to the total population from the GVB pairs will also be given, since the major shifts of charge are reflected in the GVB orbitals. Only the contribution from the strongly occupied natural orbital ϕ_{i1} of each pair is given, as the contribution from the weakly occupied NO (weighted by $C_{i2}{}^2$) is negligible.

Usually an *orbital charge contribution* q_A is given instead of the total electron population p_A in a given orbital. These have been defined as follows

$$q_A = p_A{}^0 - p_A$$

where $p_A{}^0$ is the orbital population in the neutral atom, and $s^{4.0}$ $p^{5.0}$ and $s^{6.0}$ $p^{10.0}$ $d^{0.0}$ populations for neutral F and S, respectively, have been used. Thus, orbital charges of +1.1 and −0.3 for sulfur p and d orbitals denote that the sulfur has ac-

Table I. Orbital Energies from Hartree–Fock Calculations on SF_2, SF_4, and SF_6[a]

	SF_2		SF_4		SF_6
E_T	−596.33629		−795.17801		−994.02875
$1a_1$	−92.1284	$1a_1$	−92.3316	$1a_{1g}$	−92.4803
$2a_1$	−26.3445	$2a_1$	−26.4140	$1t_{1u}$	−26.4003
$1b_2$	−26.3445	$1b_2$	−26.4140	$1e_g$	−26.4003
$3a_1$	−9.1215	$3a_1$	−26.3195	$2a_{1g}$	−26.4003
$2b_2$	−6.8013	$1b_1$	−26.3195	$3a_{1g}$	−9.4301
$4a_1$	−6.7990	$4a_1$	−9.3031	$2t_{1u}$	−7.1147
$1b_1$	−6.7937	$2b_1$	−6.9810	$4a_{1g}$	−1.8849
$5a_1$	−1.6861	$2b_2$	−6.9809	$3t_{1u}$	−1.7456
$3b_2$	−1.6407	$5a_1$	−6.9769	$2e_g$	−1.6882
$6a_1$	−0.9933	$6a_1$	−1.8091	$5a_{1g}$	−1.1192
$4b_2$	−0.7700	$3b_2$	−1.7341	$4t_{1u}$	−0.9422
$7a_1$	−0.7555	$3b_1$	−1.6422	$1t_{2g}$	−0.8562
$2b_1$	−0.7539	$7a_1$	−1.6251	$1t_{2u}$	−0.7493
$1a_2$	−0.7075	$8a_1$	−1.0808	$3e_g$	−0.7492
$5b_2$	−0.6702	$4b_2$	−0.8767	$5t_{1u}$	−0.7337
$8a_1$	−0.6072	$4b_1$	−0.8736	$1t_{1g}$	−0.7037
$3b_1$	−0.4104	$9a_1$	−0.8621		
		$1a_2$	−0.8076		
		$10a_1$	−0.7487		
		$5b_2$	−0.7476		
		$5b_1$	−0.7441		
		$6b_2$	−0.6753		
		$11a_1$	−0.6750		
		$6b_1$	−0.6679		
		$2a_2$	−0.6619		
		$12a_1$	−0.5250		

[a] Total energies (E_T) are also given.

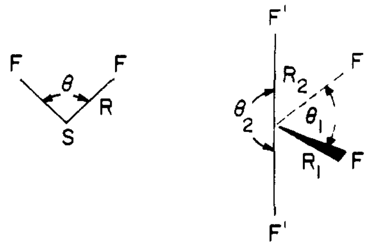


Figure 1. Structural parameters for SF_2 and SF_4.

Table II. Characteristics of the GVB Orbitals in the S Atom, SF_2, SF_4, and SF_6

GVB pair	Description	Pair energy, au	Overlap of GVB orbitals
	S Atom (^3P)		
3s pair	3s, 3s′ form	−0.0013	0.954
	3s, 3d form	−0.0012	0.959
3p*z* pair	3p, 3p′ form	−0.0036	0.910
	3p, 3d form	−0.0057	0.898
	SF_2		
σ lone pair	3s, 3s′ form	−0.0014	0.955
	3s, 3d form	−0.0033	0.932
π lone pair	3p, 3p′ form	−0.0033	0.917
	3p, 3d form	−0.0104	0.816
S–F bonds (2)		−0.0249	0.785
	SF_4		
S–F_{eq} bonds (2)		−0.0217	0.819
S–F_{ax} bonds (2)		−0.0223	0.802
σ lone pair	3s, 3d form	−0.0123	0.834
	SF_6		
S–F bonds (6)		−0.0247	0.794

quired relative charges of +1.1 and −0.3 by removing 1.1 electrons from the p orbitals and adding 0.3 electron to d orbitals.

Hybridization Analysis. In contrast to the population analysis where the NO form of the GVB wave function was used, the GVB orbitals themselves are analyzed to determine the type of hybridization the S atom is using in its bonding, since this conforms most closely with the original VB formulation of hybrid orbitals. For a S–F bond, for example, one GVB orbital ϕ_a is localized primarily on a F and the other orbital ϕ_b contains practically all the contributions from S with additional contributions from F. The contributions of the valence s, p, and d functions on S to the orbital ϕ_b are then analyzed to determine the fraction (f_i) of s, p, and d character in the sulfur component of the orbital, where the sum of the fractions ($f_s + f_p + f_d$) is equal to unity.

We stress that the population and hybridization analysis are to be viewed as a *qualitative* interpretation of the electronic structure, with less emphasis placed on the precise values themselves.

CI Calculations. In addition to the GVB calculations configuration interaction calculations (GVB-CI) were carried out in the subspace spanned by the GVB orbitals. The GVB-CI wave functions provide a more quantitative description of bond energies since they remove the restrictions of perfect pairing and strong orthogonality between pairs inherent in the GVB wave functions. All single and double excitations were included relative to the Hartree–Fock-like configuration of the dominant GVB natural orbitals. The core orbitals of S (1s, 2s, 2p) and F (1s, 2s) were held doubly occupied. For SF_2 the GVB-CI calculations involved 12 orbitals and 163 spin eigenfunctions; for SF_4, 18 orbitals and 592 spin eigenfunctions; for SF_6, 24 orbitals and 853 spin eigenfunctions.

Results of the GVB Calculations

In the following sections we discuss the successive formation SF_2, SF_4, and then SF_6 in light of the results of the GVB calculations. The orbitals of each molecule are related to the orbitals of the simpler fragments from which it is formed. Many of the results are summarized in Tables I–VII. These include energies from Hartree–Fock calculations (Table I), the overlaps and pair energies of the GVB orbitals (Table II), total energies and heats of reaction for various levels of calculation (Tables III and IV), population and hybridization analyses of the GVB pairs (Tables V and VI), and population analyses of the Hartree–Fock wave functions (Table VII).

Hartree–Fock Calculations. The orbital energies and total energies for SF_2, SF_4, and SF_6 are presented in Table I. The highest occupied orbital in SF_2 is the $3b_1$ ($\epsilon_i = -0.4104$) orbital which describes the π lone pair on sulfur. The next levels ($8a_1$ and $5b_2$) arise from the σ lone pairs. In SF_4 the highest orbital ($12a_1$ with $\epsilon = -0.5250$) corresponds to the σ nonbonding orbital on sulfur with appreciable antibonding character from the axial fluorines.

The trends in the calculated fluorine 1s binding energies are well represented in comparison with recent experimental measurements, although the absolute binding energies are ~20 eV too large. In SF_4 the equatorial 1s fluorine electrons are bound 2.6 eV more strongly (718.7 vs. 716.1 eV) in these calculations than the 1s electrons of the axial fluorines, which have more negative charge (Table VII). The measured ESCA spectrum by Shaw, Carroll, and Thomas[43] similarly shows a splitting of 2.4 eV (695.3 and 692.9 eV). Also the average fluorine 1s binding energy increases by 0.8 eV in going from SF_2 to SF_4 (716.8 to 717.6) and again by 0.8 eV from SF_4 to SF_6 (717.6 to 718.4). Although there are apparently no experimental results on SF_2, an increase of 0.5 eV is observed between the average value of 694.1 eV in SF_4[43] and the value of 694.6 in SF_6.[44]

Table III. Calculated Total Energies (au) for Sulfur Fluorides[a]

Calculation	Energy
$S(^3P)$	
HF	−397.469 04
GVB (2)	−397.475 97
SF_2	
HF	−596.336 29 (−596.372 36)
GVB (4)	−596.395 15 (−596.429 44)
GVB-CI	−596.417 44 (−596.451 03)
SF_4	
HF	−795.178 01
GVB (3), S-F_{eq} and σ lone pairs	−795.232 96
GVB (2), S-F_{ax} pairs	−795.221 19
GVB (5)	−795.267 0[b]
GVB-CI	−795.291 57
SF_6	
HF	−994.028 75
GVB (1)	−994.052 98
GVB (6)	−994.145 4[b]
GVB-CI	−994.185 64
F	
HF	− 99.393 30
F_2	
HF	−198.707 48 (−198.732 24)
GVB	−198.790 20 (−198.809 33)
GVB-CI	−198.792 03 (−198.813 55)

[a] Quantities in parentheses refer to results where d functions on the F atoms were added. [b] Estimated.

Table IV. Calculated Energies for Selected Reactions of Sulfur Fluorides[d]

	Energy, kcal/mol			
Reaction	Hartree–Fock	GVB	GVB–CI	Exptl[a]
$SF_2 \rightarrow S + 2F$	51 (73)	83 (105)	97 (118)	172
$SF_4 \rightarrow SF_2 + 2F$	34	52	55	152
$SF_4 \rightarrow S + 4F$	78	130	152	324
$SF_6 \rightarrow SF_4 + 2F$	40	58	67	140
$SF_6 \rightarrow S + 6F$	125	186	220	464
$F_2 \rightarrow 2F$	−50 (−34)	2.3 (14)	3.4 (17)	36
$SF_4 \rightarrow SF_2 + F_2$	84	51	52	116
$SF_6 \rightarrow SF_4 + F_2$	90	55	64	102

[a] Based on the following $\Delta H_f°$ thermodynamic values:[b] F (18.4), S (66.1), SF_4 (−185.1), SF_6 (−288.5), F_2 (0.0), and SF_2 (−69.5).[c] [b] JANAF Thermochemical Tables, 2nd ed, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, **No. 37** (1970). [c] P. A. G. O'Hare and A. C. Wahl, *J. Chem. Phys.*, **53**, 2834 (1970). [d] Calculated quantities in parentheses refer to results where d functions on the F atoms were added. No zero-point energy corrections have been made for the experimental quantities.

Another trend evident in the results is an increase in the binding of the lowest valence electrons SF_2 compared to H_2S as given from the reported orbital energies of H_2S by Schwenzer and Schaefer.[28] The $6a_1$ orbital (ϵ = −0.993 au) in SF_2 is only slightly more bound than the $4a_1$ (−0.977) in H_2S, but the next two levels, $4b_2$ (−0.770) and $7a_1$ (−0.755), are 5 and 7 eV more strongly bound than the next two levels of H_2S, $2b_1$ (−0.594) and $5a_1$ (−0.492) in Schwenzer and Schaefer's notation. A similar stabilization of the σ orbitals in F_2O compared to H_2O the so-called "perfluoro effect", has been analyzed by Brundle, Robin, Kuebler, and Basch.[45]

Table V. Mulliken Population Analysis of GVB Orbitals Describing S–F Bonds in SF_2, SF_4, and SF_6[a]

		Population						
		S			F_{eq}		F_{ax}	
Molecules	Bond	s	p	d	s	p	s	p
SF_2	S–F		0.46	0.06	0.02	1.46		
SF_4	S–F_{eq}	0.07	0.38	0.09	0.01	1.43		
	S–F_{ax}	−0.01	0.32	0.10			0.03	1.55
SF_6	S–F	0.13	0.27	0.13		1.43		

[a] Total population in each bond is 2.0 electrons. Only populations on the two atoms involved in the bond are given.

Table VI. Analysis of S Atom Hybridization in the GVB Orbitals of the SF_n Sequence

	Fraction of sulfur component		
GVB orbital	s	p	d
S atom			
Triplet pair (3p*x*, 3p*y*)	0.00	1.00	0.00
π lone pair (3p*z*)	0.00	0.95	0.05
σ lone pair (3s)	0.98	0.00	0.02
SF_2			
S-F bonds	0.07	0.86	0.07
π lone pair	0.01	0.94	0.05
σ lone pair	0.88	0.09	0.03
SF_4			
S-F_{eq} bonds	0.15	0.71	0.14
S-F_{ax} bonds	0.04	0.84	0.12
σ lone pair	0.67	0.28	0.05
SF_6			
S-F bonds	0.34	0.51	0.15

The total energy of SF_6 from the present calculations (−994.0287) is 0.2420 hartree lower than the SCF energy reported recently by von Niessen et al.[26] (−993.7867) in the most accurate calculation to date. (The present calculations have still not converged to the Hartree–Fock limit because of the lack of polarization functions on the fluorines and other limitations of the basis set.) The ordering of the orbitals in our work agrees with the results of von Niessen et al. and of Roos[25b] but differs from the results of Gianturco et al.,[25a] who employed a less extensive Gaussian basis. The total energies from the latter two calculations were −992.9313 and −990.1283 au, respectively.

SF_2 Calculations. The ground state (^3P) of the S atom can be represented

$$a\ 3s^2 3pz^2 3px 3py\ \alpha\beta\alpha\beta\alpha\alpha \tag{3}$$

while the F atom (^2P) ground state is

$$a\ 2s^2 2pz^2 2px^2 2py\ \alpha\beta\alpha\beta\alpha\beta\alpha \tag{4}$$

SF_2 has a bond angle of 98° and fits the classical octet description of bonding. It is formed by bonding each of the two unpaired triplet orbitals of S (3p*x* and 3p*y* in (3)) with the unpaired p orbital on F (see Figure 2a).

The Hartree–Fock configuration has the form

$$\ldots 6a_1^2 7a_1^2 8a_1^2 4b_2^2 5b_2^2 2b_1^2 3b_1^2 1a_2^2$$

The two-pair GVB wave function, denoted as GVB(2), is written

Table VII. Mulliken Population Analysis of Hartree-Fock Wave Functions

	Charge contribution							Total charges		
	S			F_{eq}		F_{ax}				
	s	p	d	s	p	s	p	S	F_{eq}	F_{ax}
SF_2	0.142	0.828	−0.204	0.045	−0.428			+0.766	−0.383	
SF_4	0.307	1.767	−0.525	0.047	−0.352	0.041	−0.511	+1.549	−0.305	−0.470
SF_6	0.945	1.918	−0.952	0.044	−0.362	0.044	−0.362	+1.911	−0.318	−0.318

$$\ldots 6a_1{}^2 7a_1{}^2 4b_2{}^2 2b_1{}^2 3b_1{}^2 1a_2{}^2(\phi_{1a}\bar{\phi}_{1b} + \phi_{1b}\bar{\phi}_{1a})(\phi_{2a}\bar{\phi}_{2b} + \phi_{2b}\phi_{2a}) \quad (5)$$

where ϕ_{1a} and ϕ_{1b} are approximately (un-normalized)

$$\phi_{1a} \sim 3p_S + 2p_{F1}$$

$$\phi_{1b} \sim 2p_{F1} \quad (6)$$

i.e., they have retained their atomic-like character, but the S 3p orbital has delocalized onto the F to produce a slightly ionic bond.

This pair in the GVB natural orbital representation is described thus

$$C_1(\sigma_{S\text{-}F1})^2 - C_2(\sigma^*{}_{S\text{-}F1})^2 \quad (7)$$

where σ and σ^* represent localized bonding and antibonding orbitals, respectively for the S-F1 bond. A Mulliken population analysis of the σ_{S-F} orbital (Table V) reveals that of the 2.0 electrons in each bond 1.48 are assigned to the F resulting in a $S^{+0.48}F^{-0.48}$ polar bond.

The GVB orbitals in (4) have an overlap of 0.785 compared to 1.0 when the orbitals are required to be the same for both electrons, as in Hartree-Fock. This produces an energy lowering of 15 kcal/mol (0.0249 au) in each bond relative to Hartree-Fock (Table II). Actually the sulfur-like GVB orbital ϕ_{1a} in (1) is not purely 3p in nature. Decomposition of the valence S components in ϕ_{1a} shows it to be 86% p, with admixture of 7% and 7% d character (Table VI).

To begin to address the question of how SF_2 can bind two more fluorines to form SF_4 we must direct our attention to the lone pair electrons. In the wave function (3) let us denote the $7a_1$ and $3b_1$ orbitals as the lone pairs deriving from the S 3s(σ) and 3pz(π) orbitals, respectively. Instead of taking them to be doubly occupied one could also treat them in a GVB fashion.

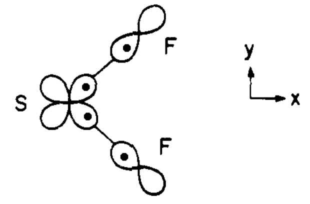
Considering the π lone pair first, one finds that there are at least two possible forms of the wave function:

$$3p_a(1)\overline{3p_b}(2) + 3p_b(1)\overline{3p_a}(2) = C_1(3p)^2 - C_2(3p')^2 \quad (8)$$

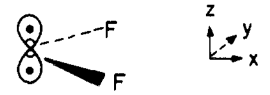
$$pd_+(1)\overline{pd_-}(2) + pd_-(1)\overline{pd_+}(2) = C_1(3p)^2 - C_2(3dz^2)^2 \quad (9)$$

where $pd_\pm = 3p \pm \lambda 3dz^2$. In the former case (8), $3p_a$ and $3p_b$ correspond to 3p-like functions which differ only in radial behavior, i.e., $3p_b$ being more diffuse than $3p_a$. This type of "in-out" radial correlation is the type one normally encounters in GVB wave functions for lone pairs of N, O, and F compounds. In the latter case (9), this type of "angular" correlation produces two 3p–3dz^2 hybrid lobes, one with more amplitude *above* the plane of the molecule, and one with the corresponding amplitude beneath the plane (Figure 2b).

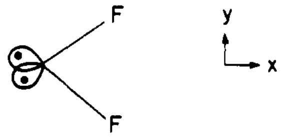
The results of the GVB calculations (Table I) give respective energy lowerings of −0.0033 and −0.0104 hartree for forms 6 and 7 relative to Hartree-Fock; i.e., the 3p–3dz^2 hybrid form is slightly preferred by −0.0071 hartree. In (8) the wave function had the form ... $[C_1(3b_1)^2 - C_2(4b_1)^2]$ for the lone pair while in (9) it had the form ... $[C_1(3b_1)^2 - C_2(8a_1)^2]$.



(A) S-F BONDS



(B) π LOBES



(C) σ LOBES

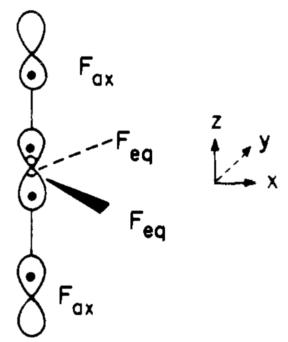
Figure 2. Schematic description of GVB orbitals in SF_2. Lines connecting lobes denote singlet coupling.

This form also allows the GVB orbitals to reduce their overlap (0.816) compared to the 3p, 3p′ form (0.917). Thus even in the isolated SF_2 molecule one sees the beginnings of possible bonds with additional atoms, as these p–d hybrids are oriented to bind atoms in the axial direction. The hybridization analysis (Table VI) shows the S components of these lobes to be 94% 3p, 5% 3d, and 1% 3s.

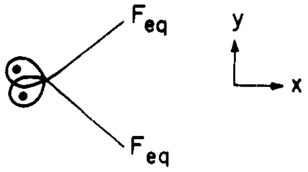
Similarly one can treat the σ lone pair in GVB, and again there are at least two distinct possibilities: the 3s, 3s′ form analogous to the above 3p, 3p′ case where one obtains 3s orbitals of different radial character, and a 3s ± λ3dxy form where one forms lobes in the plane of the molecule bent back from the S–F bonds (Figure 2c). Again the form using 3d orbitals is preferred (Table I) although the difference between them is considerably smaller (0.0019 hartree) and the resulting overlap in the preferred function (0.932) is still quite high. The s–d lobes also incorporate p character (88% s, 9% p, 3% d) to direct them away from the S–F bonds.

This tendency of the sulfur lone pairs to incorporate some 3d character to suggest incipient new bonds is also evident in the atom itself. Calculations on the S atom show the (3p, 3d) form to be preferred over the (3p, 3p′) solution (Table II) and the two forms for the 3s lone pair to be comparable. The percent d character in the GVB lone pair orbitals (Table VI) is nearly the same in the S atom as in SF_2. The overall amount of d character in all of these lone pairs is nonetheless quite small.

Having thus determined the optimum form of the lone pair orbitals, a GVB(4) calculation was then carried out where both



(A) S-F$_{ax}$ BONDS



(B) σ LOBES

Figure 3. Schematic description of GVB orbitals in SF$_4$. Lines connecting lobes denote singlet coupling. The S–F$_{eq}$ bonds, not shown, are qualitatively similar to the bonds in SF$_2$.

bonds and lone pairs were "split" into GVB pairs. In the NO form, the wave function was

$$\ldots 6a_1^2 4b_2^2 2b_1^2 1a_2^2 [C_1(7a_1^2) - C_2(5b_2^2)][C_3(3b_1^2) - C_4(8a_1^2)][C_5(\sigma_{SF_1})^2 - C_6(\sigma^*_{SF_1})^2][C_5(\sigma_{SF_2})^2 - C_6(\sigma^*_{SF_2})^2] \quad (10)$$

Finally a GVB-CI calculation was performed where all single and double excitations relative to the "Hartree-Fock" configuration $\ldots 6a_1^2 4b_2^2 2b_1^2 1a_2^2 7a_1^2 3b_1^2 (\sigma_{SF_1})^2 (\sigma_{SF_2})^2$ within the space of the 12 orbitals were defined by the GVB(4) function. The net effect of the improvements in the wave function in GVB and GVB-CI is to incorporate 32 and 46 kcal/mol binding energy relative to S + 2F compared to Hartree-Fock. The addition of d functions on the fluorine yields an additional 20 kcal/mol improvement in the energy of atomization (Table IV).

SF$_4$ Calculations. The GVB orbitals of SF$_4$ (Figure 3) resemble the orbitals of SF$_2$ in many respects. The S–F$_{eq}$ bonding orbitals in SF$_4$ are very nearly unchanged from the S–F bonding orbitals of SF$_2$. They are still quite ionic in character (Table V) with a bond polarity of $S^{+0.44}F_{eq}^{-0.44}$ in SF$_4$ compared to $S^{+0.48}F^{-0.48}$ in SF$_2$. The hybridization on the S atom (15% s, 71% p, 14% d) is also similar to that of SF$_2$ (7% s, 86% p, 7% d). The lobes of the σ lone pair have the form

$$\phi_a, \phi_b = 0.820\ 3s + 0.505\ 3p_y + 0.062\ 3d_{z^2} \pm (0.170\ 3p_x - 0.199\ 3d_{xy})$$

where the axes and the orbitals are schematically shown in Figure 3.

The bonds to the axial fluorine atoms have been formed by bonding the unpaired 2p electron of F to the p-d lobe of SF$_2$. The GVB orbital originally corresponding to the 2p$_F$ orbital has changed relatively little, while the original p-d lobe was delocalized extensively onto the F as in (4) for the S–F bonds of SF$_2$. The S–F$_{ax}$ orbitals show an accumulation of −0.57 charge on the F which is 0.13 more charge than in the S–F$_{eq}$ bonds. The overall populations of the Hartree-Fock wave function (−0.51 on F$_{ax}$ and −0.36 on F$_{eq}$) also reflect this. Previous calculations have also noted the greater ionicity of the S–F$_{ax}$ bonds.

Comparison of the π lobes of SF$_2$ and S–F$_{ax}$ bonding orbitals of S–F$_{eq}$ (Table VI) reveals only a slight increase in the percent of 3d character of the sulfur components (5% d in SF$_2$ compared to 12% d in SF$_4$). This is far less than the 50% d character one would expect if the molecule used traditional p–d hybrids

$$\phi_{pd} = (1/2^{1/2})3p \pm (1/2^{1/2})3d$$

for bonding.

In order to form bonds to the axial fluorines, the GVB lone pair orbitals must decrease their overlap. In SF$_2$, the π electron pair $\phi_a\bar{\phi}_b + \phi_b\bar{\phi}_a$ had an overlap of 0.816, where (ϕ_a, ϕ_b) are the pd$_+$ and pd$_-$ orbitals of (9):

$$\phi_a \sim 3pz + \lambda 3dz^2$$
$$\phi_b \sim 3pz - \lambda 3dz^2$$

When they become bonded to the fluorines the two bonds are written $(\phi_a\bar{\phi}_{F3} + \phi_{F3}\bar{\phi}_a)$ and $(\phi_b\bar{\phi}_{F4} + \phi_{F4}\bar{\phi}_b)$ where $\langle\phi_a|\phi_b\rangle = 0$ and similarly for the other overlaps between orbitals of different bonds. Now the GVB orbitals have the form

$$\begin{aligned}\phi_a &\sim 3pz_S + \lambda_d 3dz_S^2 + \lambda_F 2pz_{F3}\\ \phi_b &\sim 3pz_S - \lambda_d 3dz_S^2 + \lambda_F 2pz_{F4}\end{aligned} \quad (11)$$

The GVB orbitals can therefore reduce their overlap by either increasing λ_d, the percent of d character, or by increasing λ_F, the percent of fluorine character or ionicity. Although we have seen that there is a slight increase in d contribution, the most energetically favorable mechanism of reducing the overlap is the incorporation of S^+F^- character into the wave function rather than promotion of an electron into the 3d shell. The standard VB wave function, by contrast, took $\lambda_F = 0$ in ϕ_a and thus imposed the requirement of 50% d character to maintain orbital orthogonality.

The GVB wave function leads to improved bond energies and heats of reaction (Table IV). For SF$_4$ the gvb results were obtained in two stages to reduce the computational effort. In a GVB(3) calculation the orbitals for the equational bonds and σ lone pairs were first obtained. In a second calculation the axial bonds were treated in a GVB fashion by splitting the two pairs. Finally the orbitals were merged into one orthogonal linearly independent set. This process should not significantly affect the GVB analysis since the primary GVB natural orbitals from the separate calculations were very nearly orthogonal, and the least important secondary NO's had small overlaps. A GVB–CI was performed in the merged basis analogous to the previous SF$_2$ calculation. The 10 GVB orbitals and 8 F lone pair orbitals were used.

The SF$_4$ → SF$_2$ + 2F Reaction. To gain a greater understanding of the changes occurring in the bonding of SF$_4$ the following idealized reaction was studied. Starting with the equilibrium geometry of SF$_4$, the S–F$_{ax}$ bond lengths were varied symmetrically from 2.75 to 6.0 bohr (R_e = 1.646 Å = 3.11054 bohr) while keeping all the other geometrical parameters fixed. The resulting "product" SF$_2$ molecule will thus have a very slightly different geometry from the experimental geometry of SF$_2$.

Since only the axial bonds are affected, the equatorial bonds and lone pair were treated by doubly occupied Hartree-Fock orbitals. The GVB(2) function of SF$_4$ has the form

$$\ldots (11a_1)^2(6b_2)^2(5b_1)^2(2a_2)^2(\phi_{1a}\bar{\phi}_{1b} + \phi_{1b}\bar{\phi}_{1a})(\phi_{2a}\bar{\phi}_{2b} + \phi_{2b}\bar{\phi}_{2a})$$

or

$$\ldots (11a_1)^2(6b_2)^2(5b_1)^2(2a_2)^2[C_1(\sigma_1)^2 - C_2(\sigma_1^*)^2][C_1(\sigma_2)^2 - C_2(\sigma_2^*)^2]$$

Table VIII. Results of Two-Configuration SCF Calculation for $SF_4 \rightarrow SF_2 + 2F$

R(S-F_{ax}), bohrs	Total energy, hartrees	Occupation No.	
		$12a_1$	$7b_1$
2.75	−795.128 48	0.9954	0.0046
3.1105	−795.189 94	0.9904	0.0096
3.50	−795.169 56	0.9749	0.0251
4.00	−795.115 35	0.8879	0.1121
4.50	−795.103 07	0.6373	0.3627
5.00	−795.111 98	0.5481	0.4519
6.00	−795.119 08	0.5079	0.4921
∞	−795.119 86	0.5000	0.5000

where σ_1 and $\sigma_1{}^*$ describe one axial SF bond, and σ_2 and $\sigma_2{}^*$ describe the other. These orbitals can be expanded in terms of symmetry functions

$$\sigma_1, \sigma_2 = (12a_1 \pm 6b_1)/2^{1/2}$$

$$\sigma_1{}^*, \sigma_2{}^* = (13a_1 \pm 7b_1)/2^{1/2}$$

An analysis of the wave function for SF_4 and separated $SF_2 + F + F$ in terms of the symmetry function shows that there will be two important configurations over the range of internuclear separations with smaller contributions from the others.

These important two configurations are the Hartree-Fock configuration

$$\ldots(11a_1)^2(6b_2)^2(5b_1)^2(2a_2)^2(6b_1)^2(12a_1)^2$$

and the configuration

$$\ldots(11a_1)^2(6b_2)^2(5b_1)^2(2a_2)^2(6b_1)^2(7b_1)^2$$

A two-configuration SCF calculation was therefore selected as having the simplest form for studying the symmetric dissociation of SF_4 into $SF_2 + 2F$, where the orbitals and relative weights of the two configurations were optimized for seven selected distances. The energies are given in Table VIII along with the occupation numbers of the $12a_1$ and $7b_1$ orbitals.

The resulting potential energy curve (Figure 4) shows that as the fluorines approach at large internuclear separations there is initially a repulsive interaction. Eventually the repulsive barrier (~10 kcal) is overcome by an attractive interaction which binds the F atoms relative to $SF_2 + 2F$ by 44 kcal. This is much smaller than the experimental heat of reaction (155 kcal) because other correlation effects have not been included and also because 3d polarization functions on the fluorine are not present in the basis.

The analysis of the charge distributions in this process is quite striking (Tables IX and X). Consistent with our earlier analysis the total 3d population increases modestly from 0.24 to 0.51 electron. However, 0.50 electron is transferred to each fluorine atom, as depicted in Figure 5. As shown in the figure the charge transfer occurs quite sharply over a distance of 4 to 4.5 bohrs.

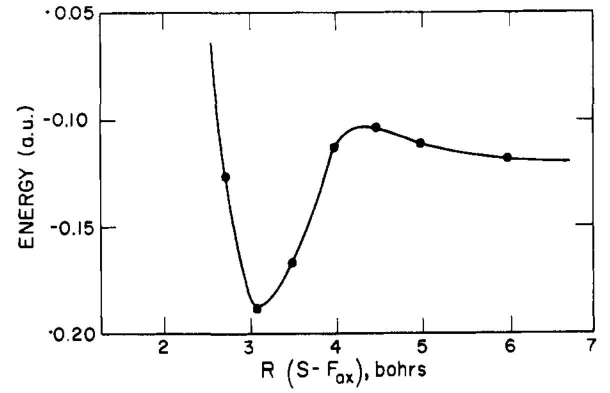


Figure 4. Calculated potential energy curve for the model reaction $SF_4 \rightarrow SF_2 + 2F$.

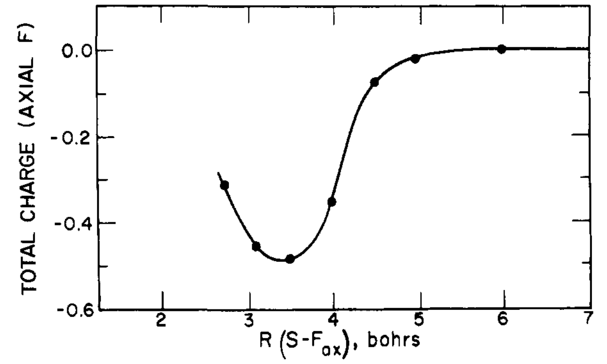


Figure 5. Total charge on each axial fluorine as a function of S-F_{ax} bond length in the $SF_4 \rightarrow SF_2 + 2F$ reaction.

This is suggestive of a mechanism schematically indicated in Figure 6. As the F's approach on a relatively flat potential energy surface, the curve is crossed by the attractive $SF_2{}^+ + F^- + F$ ionic curve (see Figure 6). The unpaired electron on $SF_2{}^+$ can bond to the fluorine to form the classical $SF_3{}^+$ molecule isoelectronic with PF_3. The ion-pair attraction between $SF_3{}^+$ and F^- plus the resonance energy between $F^-\ SF_2{}^+\text{-}F$ and $F\text{-}SF_2{}^+\ F^-$ can account for the stabilization of the fourth SF bond.

To obtain a rough estimate of where the ionic curve would be expected to cross the covalent curve, the orbital energy ϵ_i of the doubly occupied $3p_z$ orbital (−0.3914) in the ^3P state of S ($3p_z{}^23p_x3p_y$) was used in the expression

$$IP = -\epsilon_i + 2K_{pp'} + \Delta\epsilon_{corr}$$

Table IX. Mulliken Population Analysis of Two-Configuration SCF Calculation for $SF_4 \rightarrow SF_2 + 2F$[a]

R(S-F_{ax}), bohrs	F_{eq}		S			F_{ax}	
	s	p	s	p	d	s	p
2.75	0.05	−0.40	0.32	1.70	−0.71	0.08	−0.39
3.1105	0.05	−0.35	0.30	1.74	−0.51	0.04	−0.50
3.50	0.05	−0.32	0.26	1.67	−0.39	0.02	−0.52
4.00	0.05	−0.33	0.20	1.37	−0.29	0.01	−0.37
4.50	0.05	−0.39	0.17	0.91	−0.25	0.01	−0.09
5.00	0.05	−0.40	0.15	0.82	−0.24	0.00	−0.02
6.00	0.05	−0.41	0.15	0.81	−0.24	0.00	−0.00

[a] The charge contributions denote the difference in populations between the neutral atoms and the molecule, where $s^{4.0}p^{5.0}$ and $s^{6.0}p^{10.0}d^{0.0}$ configurations have been used for F and S, respectively.

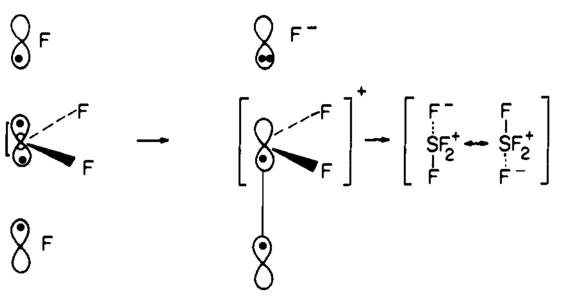


Figure 6. Idealized representation of GVB orbitals in the $SF_4 \rightarrow SF_2 + 2F$ reaction.

Table X. Atomic Charges in the $SF_4 \rightarrow SF_2 + 2F$ Reaction

	Total charge		
$R(S\text{-}F_{ax})$, bohrs	S	F_{eq}	F_{ax}
2.75	1.322	−0.349	−0.305
3.1105	1.530	−0.307	−0.457
3.50	1.545	−0.276	−0.497
4.00	1.277	−0.281	−0.358
4.50	0.834	−0.338	−0.083
5.00	0.739	−0.351	−0.019
6.00	0.714	−0.355	−0.003

Using experimental values for the IP (10.36 eV) and $E(^1D) - E(^3P) = 1.12$ eV $= 2K_{pp'}$ for the exchange integral, $\Delta\epsilon_{corr}$ was found to be −1.41 eV. Then taking ϵ_i of SF_2 (−0.4104) this led to an estimated IP of 9.76 eV for SF_2. The crossing point can then be calculated as $R_x = 27.21/(IP(SF_2) - EA(F)) = 4.3$ bohrs by inserting 3.40 eV for the electron affinity[36] of F. This distance, larger than the equilibrium distance of 3.11 bohrs, suggests that the ionic states could easily play an important role in the binding.

Because of the "resonance" interaction between the forms in Figure 6, the GVB orbitals in SF_4 becomes equivalent instead of the asymmetric forms indicated in the figure.

These results are qualitatively similar to the conclusions from recent calculations[37] on KrF_2 and XeF_2, where the bonding was described as $F^-Xe^+F \leftrightarrow FXe^+F^-$. This is also very close to the models suggested by Coulson[11] and Pitzer[12] for the electronic structure of the hypervalent systems. Bagus et al.[37] also found a barrier for the symmetric approach of two fluorines to the rare gas at the two-configuration level. Inclusion of other correlation effects removed the barrier and improved the binding energy. It is therefore likely that the barrier in Figure 4 may also be removed by electron correlation. This would not affect the arguments advanced here concerning the importance of ionic character.

SF_6 Calculations. Since the six bonds in SF_6 are equivalent, the GVB bonding and antibonding orbitals from a 1-pair calculation were rotated to form the pairs for the six bonds. An estimate of the GVB(6) energy was made from the pair energies and pair-pair repulsions. The rigorous GVB-CI energy was calculated from a wave function including all (1 + 2) excitations relative to the Hartree-Fock-like configuration in the space of the 12 GVB orbitals and the 12 F lone pair orbitals.

The population analysis shows an increase in the percent s character in the bonds (a total of 0.78 electron for all bonds in SF_6 compared to approximately 0.14 in SF_4). This is not surprising since the final bonds were formed by bonding the fluorines to the lone pair of SF_4 which had predominantly s character.

The overall 3d population has also increased from 0.36 electron in all SF_4 bonds to 0.78 electron in all the SF_6 bonds.

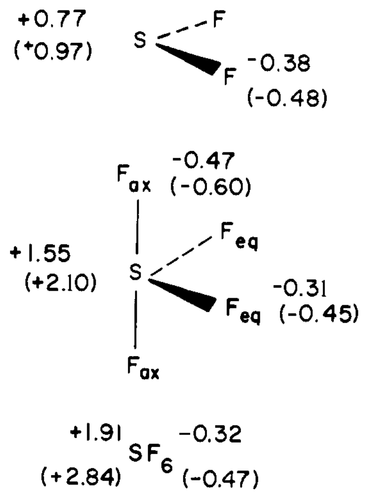


Figure 7. Charge distributions in SF_2, SF_4, and SF_6. Shown beside each atom is the net charge from a Mulliken population analysis of the Hartree-Fock wave function. In parentheses are shown the contributions to the total charge distribution from the GVB orbitals describing the S-F bonds.

The hybridization of the GVB orbital with sulfur components (34% s, 51% p, and 15% d) is markedly different from the sp^3d^2 hybrids of VB theory

$$\phi_{sp^3d^2} = (1/6^{1/2})3s + (1/2^{1/2})3p_z + (1/3^{1/2})3d_{z^2}$$

with 17% s, 50% p, and 33% d.

This again suggests that the bonding of two more fluorines is facilitated not so much by the use of 3d orbitals but rather through charge transfer from the S to the F. In Figure 7, the overall atomic charges from Hartree-Fock calculations are shown for SF_2, SF_4, and SF_6. In parentheses are given the charges obtained from considering just the GVB S-F bonding orbitals. These were obtained by subtracting the populations in the bonding orbitals from atomic populations, where a single 2p electron was assumed for the F and a $3p^2$ configuration for S in SF_2, $3p^4$ in SF_4, and $3s^23p^4$ in SF_6.

The σ orbital contribution suggests that 0.76 additional electron has been transferred to the fluorines in going from SF_4 to SF_6. The overall charge distribution shows a net transfer of only 0.37 electron, implying that π donation from the F back to the S partially cancels the effect. The previous exercise on SF_4 would suggest the following sequence leading to SF_6

$$SF_4 + F + F \rightarrow SF_4^+ + F^- + F \rightarrow SF_5^+ + F^- \rightarrow SF_6$$

or alternatively

$$SF_4 + F + F \rightarrow SF_4^+ + F^- + F \rightarrow SF_5 + F \rightarrow SF_6$$

where in either case a net transfer of approximately 1 electron is required.

In the analogous case of the rare gas halides the possibilities are

$$Xe + F + F \rightarrow Xe^+ + F^- + F \rightarrow XeF^+ + F^- \rightarrow XeF_2$$

or

$$\rightarrow XeF + F \rightarrow XeF_2$$

Since it appears the neutral monohalides such as XeF have at most a few kilocalories per mole of binding energy,[38] the ion-pair recombination energy is not sufficient to overcome (IP − EA) in the latter case. In general, the radical neutral species (SF_3, SF_5, XeF) have the more unfavorable situation of a three-electron "half bond" compared to the closed shell species (SF_4, SF_6, XeF_2) which have essentially one covalent bond, one ionic bond, plus some resonance energy.

Table XI. Molecular Properties of SF_2 and SF_4 (the following properties are all identically zero for SF_6)

Property	Hartree-Fock	GVB-CI	Exptl
	SF_2		
Dipole moment, D[d]	−2.15	−1.78	$\lvert\mu\rvert = 1.05$[a]
Quadrupole moment, (10^{-26} esu cm^2)[e]			
θ_{xx}	−2.32	−1.79	
θ_{yy}	1.87	1.93	
θ_{zz}	0.050	−0.143	
Electric field gradient at S nucleus, au			
q_{xx}	−3.77	−3.53	
q_{yy}	−1.77	−1.64	
q_{zz}	−5.55	5.17	
	SF_4		
Dipole moment, D	−1.35	−1.17	$\lvert\mu\rvert = 0.632 \pm 0.003$[b]
Quadrupole moment, 10^{-26} esu cm^2			
θ_{xx}	3.64	3.39	0.6 ± 3.1[c]
θ_{yy}	5.39	4.74	10.1 ± 4.4
θ_{zz}	−9.03		−10.7 ± 2.8
Electric field gradient at S nucleus, au			
q_{xx}	−1.54	−1.48	
q_{yy}	2.44	2.27	
q_{zz}	−0.904	−0.791	

[a] Reference 32. [b] Reference 33. [c] R. G. Stone, H.G. Tigelaar, and W. H. Flygare, *J. Chem. Phys.*, **53**, 3947 (1970). [d] 1 au = 2.541 58 D [e] 1 au = 1.344 92 × 10^{-26} esu cm^2.

Molecular Properties. Selected molecular properties were computed to provide additional information on the charge distributions in the sulfur fluorides (Table XI). The calculated dipole moments of SF_2 and SF_4 are both too negative (where $\mu < 0$ corresponds to S^+F^-) indicating an overemphasis of ionic character. The GVB-CI wave functions reduce the ionic contributions, as is evident from the smaller dipole moments, which are still too large (by 0.7 and 0.5 D, respectively) compared to the experimental values. It is probable that the experimental moments are negative in agreement with the theoretical determinations. Both the theoretical and experimental results show a smaller dipole moment for SF_4. As we have seen before (Figure 7) the S is actually more positively charged in SF_4, but the majority of the charge has been transferred to the axial fluorines which contribute very little to the dipole moment. This in turn makes it less favorable to transfer charge to the equatorial fluorines. The addition of d functions on the fluorine leads to a still smaller dipole moment for SF_2 (−1.75 D for Hartree-Fock, −1.43 D for GVB-CI) in closer agreement with the experimental value ($\lvert\mu\rvert$ = 1.05 D).

The quadrupole moments of SF_4 calculated relative to the center of mass are in reasonable agreement with the range of values permitted by the experimental uncertainties. (In SF_2 the molecule was chosen to lie in the xy plane with the y axis bisecting the fluorines. The equatorial fluorines of SF_4 lie in the xy plane and the y axis again bisects the fluorines.) The large negative θ_{zz} value suggests substantial charge accumulation on the axial fluorines.

Discussion and Summary

To summarize the results of the GVB calculations on the SF_n series, the SF_2 molecules form two covalent (but highly polar) S-F bonds with the unpaired p orbitals of the respective atoms. SF_4 can be viewed as having one covalent and one ionic bond formed from bonding the unpaired F 2p orbitals to the π lone pair of SF_2. Although the GVB orbitals of this lone pair incorporate some 3d character in an attempt to form p-d hybrids, the percent d character is not substantial (5% in the SF_2 lone pair and 12% in the S-F_{ax} bonds from the hybridization analysis). Rather it is the 1.1 units of charge transferred to the axial fluorines in the S-F bonds (Figure 7) that provide the overall driving force for the stability of the species. Similarly one can consider SF_6 as being formed by bonding two F's to the σ lone pair of SF_4 with roughly another electron transferred from the S in the process. The GVB orbitals of the S-F bonds in all these molecules show extensive delocalization (~0.5 electron in each bond) onto the fluorine.

These results, which do not show any particular necessity for invoking expansion of the valence shell to include α orbitals, are in rather close agreement with the ideas of Coulson[11] and Pitzer[12] for accounting for the stability of the rare gas halides. As they and others have suggested, a low ionization potential and an electronegative ligand are the principal requirements for chemical stability.

Although this investigation has focused primarily on the nature of the bonding in these molecules for their equilibrium geometries, some observations on the nature of the preferred geometries can be made. The near linear F_{ax}-S-F_{ax} linkage in SF_4 would be favored by considering either the maximum overlap of the fluorine orbitals with the sulfur 3p orbital or by minimum repulsion of the electronegative axial fluorines. The presence of the σ lone pair prevents any distortions toward a tetrahedral structure while in SF_6, where there are no remaining lone pair electrons on the sulfur, the most symmetrical structure is favored.

An analysis of the relative importance of these effects will not be attempted at this stage, but large charge transfer to the ligands in the present calculations would undoubtedly make repulsion of the atoms an important factor. It is also consistent with the general success of electron pair repulsion theory[42] in predicting geometries and with Musher's observation[16] that in molecules where the central atoms do not have any valence nonbonding electrons (type II hypervalent molecules) the most symmetrical structure is assumed. There is little evidence from these results, on the other hand, to support Musher's scheme of hypervalent bonding involving nonorthogonal hybrid orbitals.

To indicate how one might visualize forming other hypervalent molecules, the likely form of the GVB orbitals in SOF_2 and SOF_4 is shown schematically in Figure 8. Instead of using ground state ^3P oxygen atoms with configuration

$$2s^22px^22py2pz$$

which cannot yield a singlet SOF_2 molecule when combined

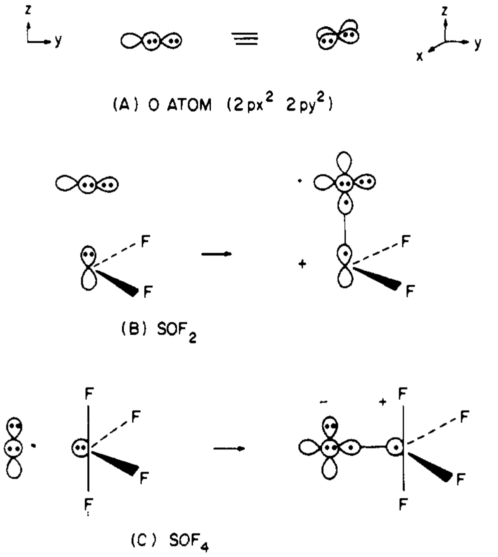


Figure 8. Schematic description of the GVB orbitals in SOF$_2$ and SOF$_4$.

with SF$_2$, the configuration

$$2s^2 2px^2 2py^2$$

is used as a starting point. This is a linear combination of $\frac{2}{3}$ (^1D) + $\frac{1}{3}$ (^1S) oxygen states and gives the most favorable interaction when the empty 2pz orbital is oriented toward the π lone pair of SF$_2$. As the S-O distance decreases, charge transfer to the oxygen becomes more favorable in analogy with our SF$_2$ + 2F model before. Similarly SOF$_4$ can be viewed (Figure 8c) as donation of charge from the σ lone pair of SF$_4$ to the oxygen.

An analogous picture emerges from recent calculations[40] on XeO which indicate that it owes its stability ($\sim$0.7 eV) to the incorporation of Xe$^+$O$^-$ character.

The apparent nonexistence of compounds such as SH$_2$F$_2$ and SH$_2$F$_4$ can be ascribed to the greater ease of charge transfer to fluorine than to hydrogen. In the hypothetical process $SF_2 + 2H \rightarrow SF_2^+ + H + H^- \rightarrow H\text{-}SF_2^+ + H^- \rightarrow SH_2F_2$ analogous to the SF$_2$ + 2F process discussed earlier the intermediates are clearly less stable in the case involving hydrogen due to the 2.6 eV greater electron affinity of fluorine. It is not so obvious, however, why the sequence $H_2S + 2F \rightarrow SH_2F_2$ cannot be envisaged. In eq 11 it was shown that the formation of two new orthogonal bonds was facilitated by charge transfer to the axial fluorines. The axial and equatorial bonds must also be maintained orthogonal, a consideration which was neglected. In a similar way one can then extend the argument to conclude that charge transfer to the equatorial fluorine is also helpful in bond formation and that such stabilization is absent in the latter sequence.

While d functions on sulfur improve the wave function, the conclusion that they are not crucial for a qualitative understanding of the overall stability of the molecule is consistent with results on other systems.[37] The d functions apparently do play a significant role in determining the geometrical structure of AB$_4$ molecules, where the differences between C_{2v}, C_{4v}, and D_{4h} structures can be small. In ClF$_4^+$, which is isoelectronic with SF$_4$, a double ζ basis predicts a C_{4v} structure while inclusion of d functions on Cl leads to a C_{2v} geometry very similar to SF$_4$.[41] Similar difficulties were encountered for SH$_4$.

In addition to providing qualitative insights into the bonding in the hypervalent systems, the GVB wave functions lead to improved quantitative descriptions of such properties as bond energies (Table III). Generally one obtains 10-20 kcal/mol additional binding energy in the S-F bonds when one proceeds from a Hartree-Fock to GVB description. Since energies of reactions are particularly difficult to compute when there are a different number of bonds in the reactants and products; a truly quantitative treatment would require larger basis sets and a more extensive CI treatments than the present ones.[42]

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