

# A Molecular Orbital Study of Bond Energies in Compounds of Sulfur and Fluorine

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CNDO/2 molecular orbital theory is employed in a study of the binding energies of the molecules SF, SF<sub>2</sub>, SF<sub>4</sub>, SF<sub>6</sub>, their cations and anions, and of the molecules SSF<sub>2</sub>, FSSF and S<sub>2</sub>F<sub>10</sub>. Computed energies, when rescaled according to energy partitioning concepts, compare favorably with available experimental data. Ionization energies and electron affinities are calculated for SF, SF<sub>2</sub>, SF<sub>4</sub> and SF<sub>6</sub>.

Mit Hilfe der CNDO/2 Theorie werden die Bindungsenergien der SF, SF<sub>2</sub>, SF<sub>4</sub> und SF<sub>6</sub> Moleküle, von deren positiven und negativen Ionen und von SSF<sub>2</sub>, FSSF und S<sub>2</sub>F<sub>10</sub> berechnet. Die berechneten Energien stimmen gut mit experimentellen Daten überein, wenn sie nach Energieaufteilungsprinzipien wiederberechnet werden. Ferner werden die Ionisierungsenergien und Elektronenaffinitäten für SF, SF<sub>2</sub>, SF<sub>4</sub> und SF<sub>6</sub> angegeben.

## Introduction

Two easy-to-use, major semiempirical molecular orbital programs are now available on call as additional research tools for any practicing chemist with access to a sufficiently large computer: the Hoffman EHMO method [1], based on a one-electron model, and the Pople many-electron approximate SCF CNDO/2-INDO method [2]. An elegant summary (through December 1968) and critique of these and related theories and their application to organic molecules has recently been offered by Jug [3]. Additional MO approaches with emphasis on *inorganic* systems have been developed by Kaufman [4], Manne [5], Fenske and Radtke [6], Hillier [7], Brown and Peel [8], Brown and Roby [9] and Sichel and Whitehead [10]. The impetus of these investigations has been directed primarily toward improvement in theoretical framework and parameterization.

Relatively few investigators have been seriously concerned with the problem of computation of realistic molecular bond energies. Within the EHMO approach, Yeranios [11] and Pearson and Mawby [12] have proposed modifications purporting to yield improved estimates. In our own studies with EHMO theory, however, we have found no modification giving consistently credible bond energy results for a series of related molecules. The VESCF-MO studies of Brown and Peel [8] produce what appear to be significant relative bond energies in related molecules but, in an absolute sense, these are much too large. Sichel and Whitehead [10] have demonstrated that the EHMO and the Pople CNDO/2 approaches with usual parameterization grossly overestimate molecular atomization energies, and offer new parameterization and internal integral approximation schemes that significantly improve results. For relatively small molecules, these more accurate values nevertheless differ from experimental ones by at least one or two electron volts.

In an alternative approach, Wiberg [13], working within the CNDO framework, proposed new internal bonding parameters appropriate to hydrocarbons, regarded the computed atomization energies as merely relative quantities in arbitrary units, and formulated impressive least-squares linear relationships between computed and experimental atomization energies of several hydrocarbons, their radicals and ions. More recently, Ehrenson and Seltzer [14] have analyzed and justified Wiberg's results with their modification of the energy partitioning concepts previously applied by Fischer and Kollmar [15] to qualitative explanation of hydrocarbon bond energies.

Our interest in bond energy trends among several inorganic halogen molecule families and the apparent promise of the above approach prompted us to undertake a somewhat similar investigation on a large series of molecules and molecule ions of sulfur and fluorine. As we will demonstrate, a rescaling process of the sum of all CNDO/2 bicentric energy terms  $E_{AB}$ , as defined originally by Pople, can lead to theoretical bond energies of accuracy comparable to or perhaps greater than those predicted by thermochemical rationalizations.

### Experimental Details and Data

CNDO/2 calculations with unmodified Pople parameters were performed on the UNIVAC 1108 computer with the Dobosh program [2]. Additions were made to the program to permit collection of all terms  $E_{AB}$  after the terminal SCF iteration. The molecules considered were  $S_2$ , SF,  $SF^+$ ,  $SF^-$ ,  $SF_2$ ,  $SF_2^+$ ,  $SF_2^-$ ,  $SF_4$ ,  $SF_4^+$ ,  $SF_4^-$ ,  $SF_6$ ,  $SF_6^+$ ,  $SF_6^-$ ,  $S=SF_2$ , FSSF, and  $S_2F_{10}$ , with computations performed for known or estimated equilibrium geometries only.

Recent structural and thermodynamic data for these species have been reviewed in a comprehensive report by O'Hare [16]. The experimental heats of atomization quoted here were computed from heats of formation and fundamental vibrational frequencies collected or estimated in this report. Temperature corrections to 0° K were considered to be beyond our anticipated accuracy. Experimental heats of atomization (called HATX) thus refer to 25° C and include zero point energies.

Experimental data for each molecule pertinent to our discussion are reviewed below.

#### SF

The experimental dissociation energy of SF is unknown. Under the assumption that primary and secondary bond energies in  $SF_2$  are the same, O'Hare [16] made estimates of the heat of formation leading to HATX (SF) = 87.1 kcal/mole at the experimental  $R(SF) = 1.599 \text{ \AA}$  [17]. Later, with the *ab initio* BISON program, O'Hare and Wahl [18] computed  $D_0^0(SF) = 4.2 \text{ eV}$  (96.8 kcal/mole),  $I(SF) = 10.0 \text{ eV}$  and  $EA(SF) = 2.5 \text{ eV}$ . No experimental value is known for the electron affinity,  $EA$ ; however, Glemser, Muller, Bohler and Krebs [19] have estimated  $I(SF) = 12.4 \text{ eV}$  from a study of the process  $NSF + e^- = N + SF^+ + 2e^-$ , and Marriott and Cragg's electron impact studies [20] on  $SF_6$  indicate  $I(SF) \cong 14.2 \text{ eV}$ . O'Hare and Wahl have presented arguments supporting their belief that both these ionization energies are too high.

SF<sub>2</sub>

From thermochemical estimates made by O'Hare [16], HATX(SF<sub>2</sub>) = 174.8 kcal/mole. Johnson and Powell [21] have determined from its microwave spectrum that SF<sub>2</sub> is a C<sub>2v</sub> species with R(SF) = 1.589 Å, ∠FSF = 98°16'.

SF<sub>4</sub>

In a recent study of thiazyl tri- and monofluorides, O'Hare, Hubbard, Glemser and Wegener [22] pointed out that experimental values of  $\Delta H_f^0(\text{SF}_4, g)$  range from -162 to -208 kcal/mole. Previously, O'Hare [16] had favored a mean of -182.1 kcal/mole, which value has been adopted in the present work. A compatible HATX(SF<sub>4</sub>) is 330.7 kcal/mole.

The geometry of SF<sub>4</sub> is well established [23, 24]. The data used in our calculations are those of Tolles and Gwinn [23], as employed in the calculations of Brown and Peel [8]: R(SF)<sub>ax</sub> = 1.646 Å, R(SF)<sub>eq</sub> = 1.545 Å, ∠FSF<sub>ax</sub> = 87.8°, ∠FSF<sub>eq</sub> = 101.5°. Results of calculations run with data given by Kimura and Bauer [24] differed insignificantly.

SF<sub>6</sub>

From well established data [16] a value HATX = 484.5 kcal/mole can be deduced. The internuclear distance R(SF) = 1.564 Å [25] seems preferable to that employed by Brown and Peel.

S=SF<sub>2</sub> and FSSF

Geometries of these species are well known [26]. Data used in our calculations include, for S=SF<sub>2</sub>: R(SF) = 1.598 Å, R(SS) = 1.860 Å, ∠SSF = 107.5°, ∠FSF = 92.5°; for FSSF: R(SF) = 1.635 Å, R(SS) = 1.888 Å, ∠FSS = 108.3°, φ(dihedral) = 87.9°. From thermochemical arguments O'Hare [16] estimated heats of formation for both species. With these and observed fundamental vibrational frequencies, values of HATX(SSF<sub>2</sub>) = 266.3 kcal/mole and HATX(FSSF) = 258.7 kcal/mole were computed.

S<sub>2</sub>F<sub>10</sub>

The geometry of S<sub>2</sub>F<sub>10</sub> is believed to be that of two C<sub>4v</sub>SF<sub>5</sub> pyramids linked through a long S-S bond, with hindered rotation about that bond [27]. Bond distances used in our calculations are: R(SF) = 1.56 Å, R(SS) = 2.209 Å.

From three indirect  $\Delta H_f^0$  values estimated by O'Hare [16], a value HATX(S<sub>2</sub>F<sub>10</sub>) = 869.9 kcal/mole was obtained. In one of his thermochemical schemes O'Hare estimated D(SS) in the molecule to be 55 ± 5 kcal/mole with an empirical relation between force constants, bond distances and bond energies. The proposed relative weakness of this bond is substantiated by the S<sub>2</sub>F<sub>10</sub> thermal decomposition studies of Trost and McIntosh [28], indicating a S-S bond-breaking activation energy of 49.2 kcal/mole.

S<sub>2</sub>

Data employed for diatomic S<sub>2</sub> include D<sub>0</sub><sup>0</sup> = 101.0 kcal/mole [29, 30] and R(SS) = 1.889 Å [31], both of which values now appear to be well accepted.

### Calculations and Results

In our initial approach CNDO/2-based binding energies in atomic units were plotted against experimental heats of atomization HATX (see Fig. 1). An acceptable linear relationship obviously obtained for molecules with only SF bonds, but equally obviously was invalid for molecules combining both SS and SF bonds, a result indicating that a rescaling factor common to both types was inappropriate.

To assist analysis of the situation the CNDO/2 program was adapted to permit computation of all diatomic contributions,  $E_{AB}$ , to the total molecular energy, as defined by Pople and Beveridge [2] for closed shell systems:

$$E_{AB} = \sum_{\mu}^A \sum_{\nu}^B P_{\mu\nu} \{F_{\mu\nu} + H_{\mu\nu}\} + \{P_{AA}P_{BB} - P_{AA}Z_B - P_{BB}Z_A\} \gamma_{AB} + Z_A Z_B / R_{AB} \quad (1)$$

Previously Brown and Peel [8], working with their VESCF-MO theory (based on NDDO and entirely different integral approximations) defined as a "bond energy" a quantity like the first term of Eq. (1), and attempted to correlate these quantities with bond-stretching force constants. Fischer and Kollmar [15] with a modified CNDO method found that both the total bicentric energy  $E_{AB}$  and a subsidiary quantity,

$$E_{AB}^R = 2 \sum_{\mu}^A \sum_{\nu}^B P_{\mu\nu} H_{\mu\nu} \quad (2)$$

termed the resonance energy, were suitable qualitative measures of chemical bond strengths in a series of hydrocarbons; however, these authors were reluctant to compare  $E_{AB}$  directly with experimental dissociation energies. More recently Ehrenson and Seltzer [14] reexamined Wiberg's results with energy partitioning schemes and found that sums over "bond indices" defined according to Eq. (2) gave within original CNDO/2 parametrization a quite good correlation with heats of atomization. These authors furthermore (1) justified Wiberg's linear relation-

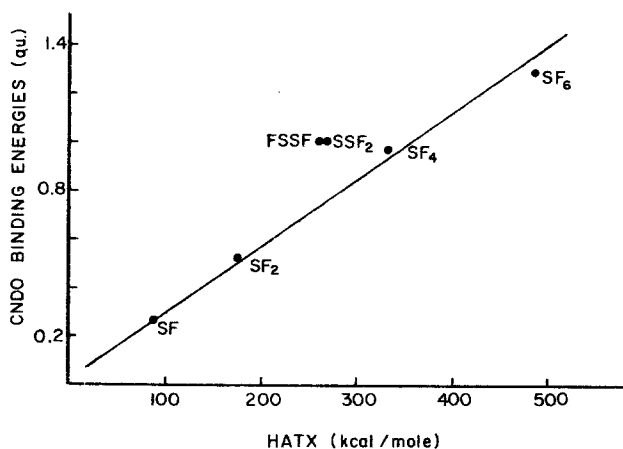


Fig. 1. Theoretical (CNDO) versus experimental (HATX) heats of atomization of sulfur-fluorine compounds

ships for many hydrocarbons including the perturbing variation in intercepts, (2) concluded that one-center contributions  $E_A$  to the total molecular energy were relatively constant per atom over a large family of hydrocarbons, (3) expressed belief that the bond index had some dependence on the  $\sigma - \pi$  character of the bond, (4) concluded that for hydrocarbons all other contributions to  $E_{AB}$  beyond those reflected in Eq. (2) either cancel or are insignificant, and (5) found that, for hydrocarbons, interactions between non-bonded AB atom pairs were negligible.

In our own analysis on compounds of sulfur and fluorine we found (1) that  $E_A$  values were sufficiently constant to justify neglect of atomic promotional energy contributions in our rescaling process, (2) that contributions to  $E_{AB}$  from terms other than  $E_{AB}^R$  amounted in some instances to 10% of  $E_{AB}^R$  (and consequently rescaling was performed on total  $E_{AB}$  values), (3) that no significant dependence of  $E_{AB}$  on single-double bond character was observed within the limits of the available experimental data, and (4) that interaction between conventionally non-bonded atoms (such as F, F) appeared to be significant when summed over the molecule.

Two rescaling procedures of partitioned  $E_{AB}$  values were considered. In method *A* only total  $E_{AB}$  values between canonically bonded atoms were considered.  $E_{SF}$  was proportionally rescaled with 1/6 HATX(SF<sub>6</sub>), the best established of experimental values, and  $E_{SS}$  was calibrated with HATX(S<sub>2</sub>) (see Table 1). Theoretical heats of atomization for all others species were obtained as appropriate sums of these quantities.

In method *B* all bicentric  $E_{AB}$  values (where AB = SS, SF and FF) were summed for each molecule, including smaller attractions and repulsions between non-bonded pairs. HATX(SF<sub>4</sub>) was used as a third calibrating factor. Results are again illustrated in Table 1.

Method *A* though yielding a less satisfactory correlation with HATX values is intrinsically somewhat more appealing, since it requires only two bonds for calibration. Furthermore it avoids, as observed in method *B*, a critical dependence of the repulsive  $E_{FF}$  interaction on the HATX values used for calibration. However, results of method *B* are much closer to estimated thermochemical values and indicate the importance of including all interactions in molecules of this type.

Since the total molecular energy is the sum over all bicentric  $E_{AB}$  and monocentric  $E_A$  terms, the success of this recalibration process (and the failure of the attempted single parameter rescaling procedure indicated in Fig. 1) establish conclusively that with the usual CNDO/2 parametrization the relative weights of bond contributions from chemically different atom pairs must be improperly reflected in the total CNDO molecular energies (and consequently in the bonding energies). Hence conclusions about geometry or conformation based on either of these quantities *for molecules of mixed-row atoms* must be suspect. On the other hand, with energy partitioning and external rescaling (or appropriate internal reparametrization) quite reasonable chemical results may be obtained.

Binding energies for the molecule ions were computed with the same rescaling factors used for neutral molecules.

Use of energy partitioning methods to estimate energies of the molecule ions permits circumvention of one problem observed during the course of this work. In the usual CNDO approach, binding energies are obtained as the difference

Table 1. Rescaled bond energies and heats of atomization

Species	$E_{\text{SF}}$ (a.u.)	$E_{\text{SS}}$ (a.u.)	Rescaled $E_{\text{SF}}$ (kcal/mole)		Rescaled $E_{\text{SS}}$ (kcal/mole)	$\Sigma E_{\text{SF}}$ (a.u.)	$\Sigma E_{\text{FF}}$ (a.u.)	Predicted heats of atomization (kcal/mole)		HATX (kcal/mole)
			Method A	Method B				Method A	Method B	
SF	-0.9079		78.4	85.2	—	-0.9079	—	78.4	85.2	87.1
SF <sup>+</sup>	-0.9940	—	85.9	93.2	—	-0.9940	—	85.9	93.2	—
SF <sup>-</sup>	-0.7362	—	63.6	69.1	—	-0.7362	—	63.6	69.1	—
SF <sub>2</sub>	-0.9226	—	79.7	86.5	—	-1.8452	+0.0095	159.4	171.1	174.8
SF <sub>2</sub> <sup>+</sup>	-0.9966	—	86.1	93.5	—	-1.9931	+0.0024	172.3	186.4	—
SF <sub>2</sub> <sup>-</sup>	-0.7655	—	66.2	71.8	—	-1.5310	+0.0254	132.3	138.4	—
SF <sub>4</sub>	-0.8874 (ax)	—	76.7	83.2	—	-3.7005	+0.0804	319.9	(330.7)	330.7
	-0.9628 (eq)	—	83.2	90.3	—					
SF <sub>4</sub> <sup>+</sup>	-0.7614 (ax)	—	65.8	71.4	—	-3.5079	+0.0243	303.2	324.1	—
	-0.9925 (eq)	—	85.8	93.1	—					
SF <sub>4</sub> <sup>-</sup>	-0.7886 (ax)	—	68.2	74.0	—	-3.2982	+0.1613	285.1	276.5	—
	-0.8605 (eq)	—	74.4	80.7	—					
SF <sub>6</sub>	-0.9342	—	80.7	87.6	—	-5.6049	+0.2022	(484.5)	(484.5)	484.5
SF <sub>6</sub> <sup>+</sup>	-0.8506	—	73.5	79.8	—	-5.1039	+0.0574	441.2	467.0	—
SF <sub>6</sub> <sup>-</sup>	-0.8555	—	74.0	80.2	—	-5.1332	+0.3832	443.7	403.4	—
S <sub>2</sub>	—	-1.4127	—	—	103.1	—	—	(103.1)	(103.1)	103.1
FSSF	-0.8736	-1.4585	75.7	81.9	106.3	-1.7624	+0.0065	257.4	270.3	258.6
SSF <sub>2</sub>	-0.8994	-1.4503	77.7	84.3	105.7	-1.8010	+0.0137	261.2	271.9	266.3
S <sub>2</sub> F <sub>10</sub>	-0.9226	-0.5687	79.7	86.5	41.5	-9.4915	+0.3601	840.9	858.3	869.9
	-0.9338 (ax)	—	80.7	87.6	—					

Parenttheses denote values used for calibration. Scaling factors are, for method A:  $1E_{\text{SS}}$  unit = 72.91 kcal/mole,  $1E_{\text{SF}}$  unit = 86.44 kcal/mole; for method B,  $1E_{\text{SS}}$  unit = 72.91 kcal/mole,  $1E_{\text{SF}}$  unit = 93.79 kcal/mole,  $1E_{\text{FF}}$  unit = 203.8 kcal/mole.

Table 2. Vertical ionization energies and electron affinities

Molecule	Ionization energies		Electron affinities	
	Method A (in eV)	Method B (in eV)	Method A (in eV)	Method B (in eV)
SF	10.0	10.0	2.8	2.8
SF <sub>2</sub>	9.6	9.7	2.3	2.0
SF <sub>4</sub>	11.1	10.6	1.9	1.1
SF <sub>6</sub>	12.2	11.1	1.7	-0.07

between total molecular energies and summed energies of isolated atoms (or ions), the latter calculated with approximations similar to those used in the total energy computation. Under these approximations, however,  $E(\text{F}^-)$  appears to be higher than  $E(\text{F})$ , leading to an incorrect description of the electron affinity process of the fluorine atom and consequent errors in binding energies of species with  $\text{F}^-$  as a dissociation product.

For  $\text{SF}^+$  and  $\text{SF}^-$ , results of both methods *A* and *B* are consistent with qualitative predictions based on increase or decrease in the number of antibonding electrons on the SF molecule.

With the computed binding energies and the experimental quantities  $I(\text{S}) = 10.357 \text{ eV}$  [32],  $EA(\text{F}) = 3.457 \text{ eV}$  [33], the ionization energy and electron affinity of SF may be computed according to the equations:

$$\begin{aligned} I(\text{SF}) &= BE(\text{SF}) + I(\text{S}) - BE(\text{SF}^+), \\ EA(\text{SF}) &= BE(\text{SF}^-) + EA(\text{F}) - BE(\text{SF}). \end{aligned} \quad (3)$$

Results obtained from rescaling methods *A* and *B* are essentially equivalent for this species:  $I(\text{SF}) = 10.0 \text{ eV}$ ,  $EA(\text{SF}) = 2.8 \text{ eV}$ , both in excellent agreement with the *ab initio* results of O'Hare and Wahl [18].

Note in Table 1 that individual SF bonds in the SF<sub>2</sub> molecule are predicted to be stronger than those in the SF radical. This most likely reflects the engagement of the antibonding odd electron on SF in an additional bond. Vertical ionization energies and electron affinities for SF<sub>2</sub> as computed from appropriate analogs of Eq. (3) are listed in Table 2.

Rescaled binding energies of ions of SF<sub>4</sub> and SF<sub>6</sub> are listed in Table 1 and vertical ionization energies and electron affinities in Table 2. In the SCF iterations on these ions the total molecular energies and density matrices converged rapidly (within 40 cycles) for all species except SF<sub>6</sub><sup>+</sup>. Although after 200 cycles a reasonable convergence of total energy resulted, a small asymmetry persisted in the density matrix. The  $E_{\text{SF}}$  value listed in Table 1 for SF<sub>6</sub><sup>+</sup> is the average over six bonds, while the sums are exact. A possible reason for the convergence difficulty may be that in the ionization process one electron is removed from the filled triply-degenerate  $3t_{1u}$  level, and small density changes are induced over the whole molecule. In contrast, no difficulty was experienced with the SF<sub>6</sub><sup>-</sup> calculation. Here the electron attached enters the non-degenerate  $3a_{1g}$  MO, markedly increasing the 3s electron density on the sulfur atom. Santry and Segal [34] have previously commented on the low occupation predicted for this orbital in SF<sub>6</sub>.

*d* orbital occupancy remains almost constant during both ionization and electron attachment processes for SF<sub>4</sub> and SF<sub>6</sub> (near 1.5 and 1.8 respectively). CNDO calculations thus do not support the suggestion of Harland and Thyne [35] that the relatively long lifetimes observed for SF<sub>4</sub><sup>-</sup> and SF<sub>6</sub><sup>-</sup> ions may be attributed to the ease with the captured electron may be accommodated in the *d* orbitals. The SF<sub>6</sub> electron affinity predicted by method *B* (close to zero) is consistent with the recent conclusions of Lifshitz, Hughes and Tiernan [36]. These authors, from studies of negative-ion charge-transfer reactions of SF<sub>6</sub>, contend that the electron affinity of this molecule is much smaller than the value 1.49 eV indicated by previous experiments [37].

Although predicted electron affinities decrease gradually from SF to SF<sub>6</sub> (Table 2), the ionization energies as calculated by both rescaling methods increase smoothly except for an interruption in the trend at SF<sub>2</sub>.

In his thermochemical analysis of the FSSF molecule, O'Hare [16], basing his arguments on the similarity of bond lengths and stretching constants, assumed equivalent bond energies for SF in FSSF and axial SF in SF<sub>4</sub>. Table 1 values roughly substantiate this assumption. *D*(SS) in FSSF was deduced to be about 20 kcal/mole lower than that in diatomic S<sub>2</sub>, and similarly *D*(SS) in SSF<sub>2</sub> was estimated at 10 kcal/mole lower than that of S<sub>2</sub>. The partitioned energies of Table 1 contradict this, indicating rather an increase in S-S bond strength in both FSSF and SSF<sub>2</sub> over that of diatomic S<sub>2</sub>. The qualitative reason for this may be much like that governing the well known fact that *D*(O<sub>2</sub><sup>+</sup>) > *D*(O<sub>2</sub>). In both these molecules electrons that were unpaired and antibonding in S<sub>2</sub> are in part drawn off by the fluorine atoms.

Within both rescaling methods the gauche *D*<sub>4*d*</sub> form of S<sub>2</sub>F<sub>10</sub> was predicted to be slightly more stable than that of the eclipsed *D*<sub>4*a*</sub> form. The energy partitioned value for the S-S bond energy (41.5 kcal/mole) is in reasonable accord with previously mentioned experimental estimates, 55 ± 5 kcal/mole [16] and 49.2 kcal/mole [28].

Calculations in progress on other inorganic halides combining first and second row atoms indicate that the methods proposed here may permit prediction of equally satisfactory values of bond energies and related properties of several important families.

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