

## AN IMPROVED ELECTRON DIFFRACTION—MICROWAVE AND MOLECULAR ORBITAL STUDY OF THE STRUCTURE OF SF<sub>5</sub>Cl

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### ABSTRACT

A new study of the structure of SF<sub>5</sub>Cl is reported. Previously-obtained electron diffraction data have been corrected for multiple scattering, and newly-reported microwave rotational constants have been combined in the analysis. Structural parameters, with estimated limits of error, were found to be  $r_g(\text{S-Cl})$  2.055(1) Å,  $r_g(\text{S-F})_{\text{mean}}$  1.570(1) Å,  $r_g(\text{S-F}_{\text{ax}}) - r_g(\text{S-F}_{\text{eq}})$  0.001(8) Å,  $r_g(\text{S-F}_{\text{eq}})$  1.571(3) Å,  $r_g(\text{S-F}_{\text{ax}})$  1.571(8) Å,  $\angle \alpha \text{ Cl-S-F}_{\text{eq}}$  90.4(0.1)°. The new data are more self-consistent than was previously the case. Ab initio molecular calculations using three different basis sets are reported and discussed.

### INTRODUCTION

SF<sub>5</sub>Cl belongs to a class of molecules whose gas-phase structure determination is deceptively difficult, and about which, in consequence, little is known. Neither electron diffraction nor microwave spectroscopy alone can provide full and precise structural data. Electron diffraction is not the method of choice for determining small differences between similar distances, such as S-F<sub>ax</sub> and S-F<sub>eq</sub> in SF<sub>5</sub>Cl, while microwave spectroscopy is in principle unable to determine the coordinates of more than one type of fluorine atom in a molecule, if these are unrelated by symmetry, since there is only one stable isotope of fluorine. Nevertheless, despite these practical difficulties, the details of the structure of SF<sub>5</sub>Cl and of related molecules are of great interest in testing the predictive power of simple models such as VSEPR theory [1] or the *trans* effect.

In a recent study of SF<sub>5</sub>Cl [2], electron diffraction and microwave data were combined in an attempt to elucidate the structure. It appeared that the axial (or *trans*) S-F bond is slightly longer than the equatorial (or *cis*), and that the Cl-S-F<sub>eq</sub> bond angle is marginally greater than 90°. These findings were supported by semi-empirical molecular orbital calculations at the extended Hückel level. Unfortunately, the structural analysis appeared

to be slightly flawed, in that the electron diffraction and microwave data did not seem to be strictly compatible or self-consistent, leading to larger uncertainties in the geometrical parameters than had been hoped.

Since the time of our original study there have been two important developments which might have relevance to this problem. Firstly, a more detailed investigation of the microwave spectrum of SF<sub>5</sub>Cl [3] yielded new, more precise rotational constants for three isotopic species, apparently significantly different from those originally reported [4]. Secondly, substantial progress has been made in developing the theory of multiple scattering in electron diffraction experiments [5, 6], to the point where corrections to intensity data which previously were ignored can now be routinely applied in structure determinations. It was decided that a re-analysis of the structural data on SF<sub>5</sub>Cl, taking advantage of these developments, would be worthwhile. We have also undertaken ab initio molecular orbital calculations on SF<sub>5</sub>Cl, using a variety of different basis sets, to provide some guide to the interpretation of the experimental results. We are unaware of any previous ab initio calculations on SF<sub>5</sub>Cl.

## STRUCTURAL ANALYSIS

Electron diffraction intensity data were originally recorded [2] at three nozzle-to-plate distances of 21, 11 and 7 cm, covering the range  $4.1 \leq s \leq 57.2 \text{ \AA}^{-1}$ . During the course of the original analysis [2], it was found that the 21 cm data appeared to be slightly inconsistent with the other two sets, and since low-angle scattering data are not crucial in the case of SF<sub>5</sub>Cl, it was decided in that work to omit the 21 cm data from the final refinements rather than run the risk of introducing systematic errors.

In the present work we performed refinements using the full set of electron diffraction data, as well as on the 11 and 7 cm sets only. Multiple scattering corrections for the 21 cm data only were made at the ITP<sub>2</sub> level following the theory outlined elsewhere [5]; corrections were applied to the 21 cm data only since the theory presently available is applicable over a limited *s*-range, and the corrections are of greatest importance at low *s*. Values for the perpendicular and parallel amplitudes of vibration needed for these corrections were taken to be those calculated from an approximate harmonic force field developed for SF<sub>5</sub>Cl as part of an earlier study [2]; shrinkage corrections and anharmonicity constants were unchanged from this work.

Although electron diffraction and microwave spectroscopy both provide structural information, data from the two experiments cannot be rigorously combined until they are transformed to a common basis. The methods for so doing are now well established [7], and in this work we adopted without change the various vibrational corrections already calculated [2]. In the joint least-squares refinement of diffraction and spectroscopic data, the corrected moments of inertia  $I_B^2$  for the three isotopic species <sup>32</sup>SF<sub>5</sub>, <sup>35</sup>Cl,

$^{32}\text{SF}_5^{37}\text{Cl}$  and  $^{34}\text{SF}_5^{35}\text{Cl}$  were assigned weights of 250, on a scale where the highest-weighted diffraction intensity point had unit weight. This weighting scheme has been justified elsewhere [2]. A weight of 10 was given to the corrected moment of inertia for  $^{34}\text{SF}_5^{37}\text{Cl}$ , since it is known with lower precision than are the moments of inertia of the other isotopic species. Diffraction intensity points were weighted according to  $s^2$ . Extensive trials [2] indicated that the structural parameters obtained were not highly sensitive to the relative weights adopted for spectroscopic and diffraction data.

All molecular orbital calculations were performed using the program GAUSSIAN 76, written by Pople and co-workers [8] and acquired from QCPE, implemented on the CYBER 170 computer installed at the University of Melbourne. Three standard basis sets were used, denoted STO-3G, STO-3G\* and STO-4-31G. Precise definitions of these terms can be found elsewhere [9]; here it suffices to say that 3G is a minimal basis set of  $s$  and  $p$  functions, 3G\* is augmented by the addition of  $3d$  functions on S and Cl, while 4-31G uses a more elaborate set of  $s$  and  $p$  functions than does 3G.

## RESULTS

### *From electron diffraction alone*

Four geometrical parameters are required to define the structure of  $\text{SF}_5\text{Cl}$ , which has  $C_{4v}$  symmetry. We chose these to be the S-Cl bond length, the mean S-F bond length, the difference  $\Delta r$  between the S-F<sub>ax</sub> and S-F<sub>eq</sub> bond lengths and the Cl-S-F<sub>eq</sub> bond angle.

All geometrical parameters refined satisfactorily, as did the amplitude of vibration for each internuclear distance. Our results obtained using the full data set from the three camera distances are presented in column I of Tables 1 and 2, and the corresponding correlation matrix is to be found in Table 3. No severe parameter correlation was found, nor was any expected since  $\text{SF}_5\text{Cl}$  is one of the rare molecules for which there are more distinct peaks in the radial distribution function than independent structural parameters. The radial distribution function derived from the 11 and 7 cm data has been published [2]; the changes caused by the addition of the corrected 21 cm data are expected to be extremely minor.

In column II of Tables 1 and 2 are displayed our earlier results obtained from the 11 and 7 cm data sets only [2]. It can be seen that no parameter differs by as much as one e.s.d., indicating that the multiple scattering corrections have made the 21 cm data compatible with the other two sets, whereas previously there had been slight inconsistencies [2]. In particular, at least for the case of  $\text{SF}_5\text{Cl}$ , the inclusion of the multiple scattering corrections has not led to appreciable changes in the refined values for the amplitudes of vibration, which remain satisfactorily close to those calculated spectroscopically.

TABLE 1

Structural results for SF<sub>2</sub>Cl<sup>a</sup>; refinement V is preferred

Parameter and Label	ED		ED + MW		V <sup>b,c,d</sup>	VI
	I <sup>b,c</sup>	II	III <sup>d</sup>	IV <sup>c,d</sup>		
r(S-Cl)	r <sub>1</sub>	2.0549 (40)	2.052 (4)	2.0553 (10)	2.0553 (10)	2.048 (3)
r(S-F) <sup>mean</sup>	r <sub>2</sub>	1.5699 (20)	1.569 (2)	1.5696 (10)	1.5700 (10)	1.570 (1)
r(S-F <sub>ax</sub> ) - r(S-F <sub>eq</sub> )	r <sub>3</sub>	-0.004 (20)	-0.003 (20)	0.006 (9)	0.004 (9)	0.022 (10)
r(S-F <sub>ax</sub> )		1.567 (16)	1.567 (16)	1.575 (6)	1.573 (6)	1.588 (7)
r(S-F <sub>eq</sub> )		1.571 (4)	1.570 (4)	1.568 (3)	1.569 (3)	1.566 (3)
∠Cl-S-F <sub>eq</sub>	∠	90.48 (0.20)	90.6 (0.2)	90.34 (0.10)	90.36 (0.10)	90.73 (0.20)
r(Cl...F <sub>eq</sub> )		2.599 (4)	2.597 (4)	2.595 (4)	2.595 (4)	2.595 (4)
r(Cl...F <sub>ax</sub> )		3.620 (16)	3.616 (16)	3.628 (7)	3.626 (7)	3.633 (9)
r(F <sub>eq</sub> ...F <sub>eq</sub> )/cis		2.222 (6)	2.220 (6)	2.219 (4)	2.220 (5)	2.214 (6)
r(F <sub>ax</sub> ...F <sub>eq</sub> )		2.210 (12)	2.205 (12)	2.216 (4)	2.216 (4)	2.217 (5)
r(F <sub>eq</sub> ...F <sub>eq</sub> )/trans		3.139 (9)	3.137 (9)	3.135 (6)	3.136 (6)	3.129 (6)
[σ(I)/I], <sup>e</sup> weight		5.9 × 10 <sup>-4</sup> , s <sup>2</sup>	6.5 × 10 <sup>-4</sup> , s	6.1 × 10 <sup>-4</sup> , s <sup>2</sup>	6.4 × 10 <sup>-4</sup> , s <sup>2</sup>	8.0 × 10 <sup>-4</sup> , s
[σ(I <sub>B</sub> <sup>2</sup> )/I <sub>B</sub> <sup>2</sup> ] <sup>f</sup>		6.1 × 10 <sup>-4</sup>	1.8 × 10 <sup>-3</sup>	9.9 × 10 <sup>-7</sup>	1.0 × 10 <sup>-6</sup>	4.5 × 10 <sup>-7</sup>

<sup>a</sup>ED = electron diffraction, MW = microwave. Units are Å for distances, and degrees for the angle. The last two entries are dimensionless. Distances are r<sub>g</sub>, the angle is ∠α. Uncertainties for pure ED refinements are 2.5σ and include estimates of systematic errors. Uncertainties for mixed ED, MW refinements are intended to be limits of error. <sup>b</sup>Incorporates corrections for intramolecular multiple scattering. <sup>c</sup>Incorporates small angle (21 cm camera) data. <sup>d</sup>Based on newer microwave data (see text). <sup>e</sup>Fractional weighted standard deviation of electron diffraction intensities. <sup>f</sup>Fractional weighted standard deviation of average moments of inertia.

TABLE 2

Amplitudes of vibration for SF<sub>5</sub>Cl, in Å<sup>a</sup>

Parameter	Label	I <sup>b</sup>	II	V	Calc. <sup>c</sup>
$l(\text{S}-\text{F}_{\text{eq}})$	$l_1$	0.045 (2)	0.044 (2)	0.045 (2)	0.043
$l(\text{S}-\text{Cl})$	$l_2$	0.051 (4)	0.050 (4)	0.051 (4)	0.048
$l(\text{Cl}\cdots\text{F}_{\text{eq}})$	$l_3$	0.070 (4)	0.067 (3)	0.070 (4)	0.070
$l(\text{Cl}\cdots\text{F}_{\text{ax}})$	$l_4$	0.063 (12)	0.062 (12)	0.063 (15)	0.057
$l(\text{F}_{\text{eq}}\cdots\text{F}_{\text{eq}})_{\text{cis}}$	$l_5$	0.061 (3)	0.060 (3)	0.061 (3)	0.063
$l(\text{F}_{\text{eq}}\cdots\text{F}_{\text{eq}})_{\text{trans}}$	$l_6$	0.059 (8)	0.057 (8)	0.059 (9)	0.054

<sup>a</sup>Refined amplitudes are  $l_g$ ; uncertainties in parentheses are  $2.5\sigma$ , and include estimates of possible systematic errors. <sup>b</sup>See Table 1 for meaning of refinements I, II and V.

<sup>c</sup>Calculated from harmonic force field discussed in ref. 2.

Although the changes in parameters between columns I and II of Table 1 are small in comparison with their uncertainties, it does appear that the new set I is the more satisfactory, since the average rotational constants calculated therefrom fit the corrected experimental constants much more closely than was originally the case. Note that the quality of fit to the diffraction data provided by refinements I and II cannot be compared directly, since  $s^2$  weighting was used for I, but  $s$  weighting for II.

#### *From combined analysis of diffraction and spectroscopic data*

Results from four different least-squares refinements are presented in columns III–VI of Table 1. Refinement III used only 11 cm and 7 cm diffraction data, but all three sets were used for both refinements IV and V, multiple scattering corrections were applied in refinement V only. For all three cases III–V we used the recent rotational constants [3] for <sup>32</sup>SF<sub>5</sub><sup>35</sup>Cl, <sup>34</sup>SF<sub>5</sub><sup>35</sup>Cl and <sup>32</sup>SF<sub>5</sub><sup>37</sup>Cl and the original constant [4] for <sup>34</sup>SF<sub>5</sub><sup>37</sup>Cl. Column V therefore presents the results which we prefer, and we take these to be the best experimental values presently available. As  $s^2$  weighting for the diffraction intensity points was used for refinements III–V, the quality of fit can be directly compared within the set I and III–V. Finally, in column VI of Table 1, we show for purposes of comparison earlier results [2] which used the original rotational constants [4] for all four isotopic species and the 11 and 7 cm electron diffraction data sets. The correlation matrix for the geometrical parameters only resulting from refinement V may be found in Table 4, while a comparison of observed and calculated (refinement V) moments of inertia for the four isotopic species of SF<sub>5</sub>Cl is displayed in Table 5.

When comparing the results of various calculations using different data sets, one must consider not only the values of the parameters but also their uncertainties. It can be seen from columns I and V of Table 1 that the

TABLE 3

Correlation matrix for SF<sub>6</sub>Cl from refinement I, ED analysis<sup>a</sup>

$r_1$	$r_2$	$r_3$	$L$	$l_1$	$l_2$	$l_3$	$l_4$	$l_5$	$l_6$	$R^b$	
$\sigma$	0.0012	0.00023	0.0049	0.065	0.00031	0.00090	0.00088	0.0041	0.0058	0.0026	0.0057
$r_1$	100	-16	-68	-18	2	-7	-1	-23	-2	-23	
$r_2$		100	24	12	7	4	1	9	2	14	
$r_3$			58	26	1	2	2	29	0	7	
$L$			100	21	-5	6	1	21	1	13	
$l_1$				100	11	18	4	31	6	63	
$l_2$					100	4	1	24	2	15	
$l_3$						100	2	10	3	30	
$l_4$							100	3	0	6	
$l_5$								100	4	40	
$l_6$									100	10	
$R$										100	

<sup>a</sup>Matrix elements given by  $P_{ij} = (M_x)_{ij} / [(M_x)_{ii}(M_x)_{jj}]^{1/2}$ , where  $M_x$  is the zeroth-order error matrix. Only the upper half of the matrix is given. All entries, except for the standard deviations, have been multiplied by 100 and rounded. Numbering of the parameters follows from Tables 1 and 2. Units for  $\sigma$  are Å for bond lengths and amplitudes of vibration, and degrees for the angle. <sup>b</sup>Index of resolution, dimensionless.

TABLE 4

Matrix of correlation coefficient for SF<sub>5</sub>Cl: refinement V, ED + MW analysis<sup>a</sup>

	$r_1$	$r_2$	$r_3$	$L$
$\sigma$	0.000096	0.00026	0.0020	0.0013
$r_1$	100	-2	-11	-29
$r_2$		100	-99	96
$r_3$			100	-92
$L$				100

<sup>a</sup>Numbering and units of parameters as in Table 3.

TABLE 5

Experimental rotational constants, vibrational corrections and comparison of experimental and calculated average moments of inertia for SF<sub>5</sub>Cl isotopic species

	<sup>32</sup> SF <sub>5</sub> <sup>35</sup> Cl	<sup>34</sup> SF <sub>5</sub> <sup>35</sup> Cl	<sup>32</sup> SF <sub>5</sub> <sup>37</sup> Cl	<sup>34</sup> SF <sub>5</sub> <sup>37</sup> Cl
Exptl. rotational constant (MHz)	1824.59248 (10) <sup>a</sup>	1823.8326 (10) <sup>a</sup>	1783.55904 (10) <sup>a</sup>	1782.70 (3) <sup>b</sup>
$B_0 - B_z$ (MHz)	0.905	0.904	0.878	0.878
Av. moment of inertia, $I_B^2$ u Å <sup>2c</sup>	277.11937 (140) <sup>d</sup>	277.23463 (140)	283.49382 (142)	283.63050 (500)
Calcd. moment of inertia (u Å <sup>2</sup> )	277.11948	277.23453	283.49373	283.63278
$\Delta$ (u Å <sup>2</sup> )	-0.00009	0.00010	0.00009	-0.00228

<sup>a</sup>Ref. 4. <sup>b</sup>Ref. 5. <sup>c</sup>A conversion factor of 505379.1 uÅ<sup>2</sup>. MHz has been used. <sup>d</sup>Uncertainty derived from experimental measurement of  $B_0$  plus assumed uncertainty of 1% in  $\Delta B_{\text{vib}}$  correction.

addition of the recent rotational constants [3] to the diffraction data has produced only modest differences in the structural parameters, with no changes as great as two least-squares standard deviations — quantities found by experience to be in general unrealistically small. Uncertainties associated with three of the geometrical parameters have decreased sharply by factors ranging from 2.4 to 12.5, with the S—Cl bond length most affected, which is to be expected since this is uniquely determined by the microwave data. Moreover, the quality of the fit to the diffraction data is scarcely affected by the incorporation of the rotational constants. All these points indicate that the diffraction data once corrected for multiple scattering and the new rotational constants [3] are quite compatible, which was not the case originally [2]. The greater correlation between the geometrical parameters resulting from the combined data set than from the diffraction data alone (compare Tables 4 and 5) might seem unexpected and momentarily puzzling, but has been rationalized elsewhere [2].

By comparing columns IV and V of Table 1, we find that the inclusion of the multiple scattering correction to the 21 cm diffraction data makes

this set more consistent with the new microwave data, since the standard deviation of the fit to the diffraction data decreases by about 8%. Although this improvement might seem modest, it is accompanied by a change in the value of  $\Delta r$ , perhaps the most interesting and certainly the least well-determined parameter of almost two standard deviations. This observation confirms previous theoretical calculations [10], which indicated that in some circumstances geometrical parameters are highly correlated with systematic errors in intensity measurements.

A comparison of columns III and VI shows that addition of the new rotational constants [3] to the diffraction data produces smaller changes in the structural parameters than did the old [4]. Although the fit to the new microwave data may not seem as good as to the old, it is still excellent, and certainly well within the presumed uncertainties inherent in the  $B_0 \rightarrow B_z$  conversion terms, tentatively assumed to be 5–10% of their magnitude. Pleasingly, the ratio of mismatch between observed and calculated average moments of inertia for  $^{34}\text{SF}_5^{37}\text{Cl}$  and that for the three other isotopic species is 25, the value expected in view of the lower weight assigned to the less precise measurement associated with the low natural abundance of this species.

Although the differences between the old [4] and new [3] rotational constants are relatively minor, no more than 3 parts in  $2 \times 10^5$ , they are not systematic, and are sufficient to alter the  $r_s$  S—Cl bond length from 2.0301 (19) Å [4] to 2.0392 (2) Å [3], a change of almost five standard deviations. This emphasizes the stringent requirements for accuracy and precision when using isotopic data to determine bond lengths. As the rotational constants for  $^{32}\text{SF}_5\text{Cl}$  and  $^{34}\text{SF}_5\text{Cl}$  differ by only 8 parts in  $2 \times 10^4$ , a precision of 1 part in  $10^6$ , equivalent to 1 kHz, is needed in the rotational constant to obtain a precision of 1 ppt in the S—Cl distance.

#### *From ab initio molecular orbital theory*

Since  $\text{SF}_5\text{Cl}$  is a moderately large molecule for full geometry optimization, the following procedure was adopted to find the minimum energy geometry, which, it is hoped, represents a reasonable compromise between the use of excessive computer time and the introduction of bias. Firstly,  $\text{SF}_6$  was studied with each of the basis sets used, and the optimum S—F bond length obtained. Results were 3G 1.649 Å, 3G\* 1.589 Å and 4-31G 1.656 Å, to be compared with the experimental  $r_g$  distance of 1.561 Å [11]. In all subsequent calculations with a particular basis set, the appropriate S—F distance was adopted as the fixed S—F<sub>eq</sub> bond length in  $\text{SF}_5\text{Cl}$ ; note that the  $r_g$  S—F distances in  $\text{SF}_6$  [11] and  $\text{SF}_5\text{Cl}$  (mean) differ by less than 0.01 Å. The S—Cl distance was fixed at the experimental  $r_g$  value of 2.055 Å, while the S—F<sub>ax</sub> bond length and the Cl—S—F<sub>eq</sub> bond angle were varied independently to minimize the molecular energy. Results are presented in Table 6. Within the limits set by the choice of basis set and the limited geometry optimiz-

TABLE 6

Molecular orbital results for SF<sub>5</sub>Cl

	3G	3G*	4-31G
Total energy (a.u.)	-1337.50475	-1338.10925	-1352.25398
Atomization energy (kcal mol <sup>-1</sup> )	-64.7	309.1	-59.3
Dipole moment (D) <sup>a</sup>	-1.77	-0.86	2.20
$r(\text{S}-\text{F}_{\text{ax}}) - r(\text{S}-\text{F}_{\text{eq}})$ (Å)	0.004	-0.002	0.006
$\angle \text{Cl}-\text{S}-\text{F}_{\text{eq}}$	91.0	89.9	91.6
Net atomic charges, <i>e</i> :			
S	1.4248	0.5779	2.1506
F <sub>ax</sub>	-0.2273	-0.0816	-0.4573
F <sub>eq</sub>	-0.2172	-0.0722	-0.4539
Cl	-0.3286	-0.2074	-0.1223
Overlap populations; $\sigma$ , $\Pi$ :			
S-F <sub>ax</sub>	0.0941, 0.0117	0.1836, 0.0977	0.0358, 0.0438
S-F <sub>eq</sub>	0.0865, 0.0122	0.1858, 0.0952	-0.0236, 0.0388
S-Cl	0.0497, 0.0039	0.2092, 0.0331	0.1448, 0.0667
total F <sub>ax</sub> ...F <sub>eq</sub>	-0.0055	-0.0070	-0.0299
F <sub>eq</sub> ...Cl	-0.0125	-0.0121	-0.0380
F <sub>eq</sub> ...F <sub>eq cis</sub>	-0.0057	-0.0070	-0.0210
Relative calculation time	1.0	6.7	5.4

<sup>a</sup>The sign is that of the Cl end of the dipole.

ation feasible, the geometrical parameters varied have converged to better than 0.002 Å or 0.1°, respectively.

It may be seen from Table 6 that the spread in values for the bond length split  $\Delta r$  predicted by the three basis sets used roughly covers the experimental uncertainty in that parameter, and that there is no unanimity even as to its sign. For the Cl-S-F<sub>eq</sub> bond angle the spread in predicted values is much greater than the experimental uncertainty, and again there is no consensus as to whether the angle is greater or less than 90°. Thus the results reported here do not support the view, frequently expressed, that ab initio calculations are more suitable in elucidating small differences between related geometrical parameters than are experiments, and it seems that a much more elaborate basis set would be necessary than was feasible here before one could have much confidence that the theoretical treatment could improve our knowledge of the structure of SF<sub>5</sub>Cl.

Values of quantities used to interpret and understand electronic structure, such as overlap populations, net atomic charges or the dipole moment, are found here to be exceptionally sensitive to the choice of basis set. Naturally one wishes to know which of the three basis sets used gives "the best" results, but there is no simple answer to this question. 4-31G leads to a much lower energy than the other two, and is thus "better" in at least some aspects. Yet comparison of the calculated atomization energies shows that only 3G\* predicts SF<sub>5</sub>Cl to be a stable molecule. We have been unable to find thermochemical data on SF<sub>5</sub>Cl, but by comparison with results available for SF<sub>6</sub> [12], the atomization energy of SF<sub>5</sub>Cl almost certainly lies in the range 400–450 kcal mol<sup>-1</sup>. Pople and co-workers have already shown [13] that inclusion of 3*d* orbitals in the basis set is essential to obtain even semi-quantitative agreement with experimental heats of atomization for hyper-

valent compounds of P, S and Cl. Comparison of the bond lengths calculated for SF<sub>6</sub> by the three basis sets shows that 3G\* is much more satisfactory in this respect than either 3G or 4-31G, and that the large improvement in energy produced by 4-31G is not matched by an improvement in calculated geometry.

The experimental value of the dipole moment for SF<sub>5</sub>Cl is 0.51 D [14]. Unfortunately its sign is not known, but both naive chemical intuition and chemical properties [15] suggest that the Cl atom is the positive end of the dipole. None of the basis sets predicts a dipole moment close to +0.51 D. While direct observation of the "net atomic charges" is of course not possible, charges on S of +1.14e in SF<sub>6</sub> and +1.07e in SF<sub>5</sub>Cl have been inferred [16] from a study of X PES. These values are not close to that predicted by the most elaborate molecular orbital calculation on SF<sub>6</sub> of which we are aware [17]; Hay found the charge on S to be +1.91e, with a 3d population on S of 0.78e. Much larger 3d populations of 1.63e in SF<sub>6</sub> and 1.52e in SF<sub>5</sub>Cl (but only 0.04e for Cl) were obtained from the present 3G\* calculations, indicating that the 3d orbitals in 3G\* are to some extent overcoming the deficiencies of the s and p basis set, although the pronounced influence of the 3d orbitals on calculated geometry and binding energy shows that the effect of their inclusion is beneficial.

A comparison of the results presented in Table 6 with those obtained assuming a "standard" geometry, in which all S—F bond lengths were equal and all bond angles of 90° is salutary, and emphasizes the importance of performing calculations at energy minima rather than assumed geometries. For example, the 4-31G basis set calculates the net atomic charge on F<sub>ax</sub> to be less negative than that on F<sub>eq</sub> at the standard geometry, but more negative at the final geometry, and the dipole moment calculated at the standard geometry is only 1.60 D.

## DISCUSSION

We have shown that in SF<sub>5</sub>Cl the S—F<sub>ax</sub> and S—F<sub>eq</sub> distances differ by no more than a few thousandths of an Ångstrom, but we are unable, either from the experimental data available or from the relatively crude ab initio molecular orbital calculations we have performed, to deduce which bond is the longer. Experimental results show the Cl—S—F<sub>eq</sub> angle to be just a few tenths of a degree greater than 90°, but here the direction and magnitude of the deviation from the idealized value of 90° are well established. Predictions of the structure of SF<sub>5</sub>Cl based on VSEPR theory [1] have been discussed at some length elsewhere [2, 18]; here we note only that the "primary" and "secondary" effects on the S—F bond lengths are finely balanced. An elementary consideration of the influence of the *trans* effect in SF<sub>5</sub>Cl indicates that F<sub>ax</sub> should withdraw more charge from the 3p<sub>z</sub> orbital on S than does Cl (the four-fold axis lies along the z direction), leading to a shortening of the S—F<sub>ax</sub> bond relative to S—F<sub>eq</sub>, but no predictions can be made about the Cl—S—F<sub>eq</sub> angle.

While many features of the molecular orbital calculations vary appreciably from basis set to basis set, there are some points common to all three sets used. In each case,  $F_{ax}$  is predicted to be more negative than  $F_{eq}$  and  $3p_z$  on S to contain more charge than  $3p_x$  or  $3p_y$ ; both these factors match the simple predictions of the *trans* effect, although both the 3G and 3G\* basis sets lead to greater negative charge on Cl than on  $F_{ax}$ , which appears contrary to chemical intuition. Overlap populations for S- $F_{ax}$  are calculated by each basis set to be greater than for S- $F_{eq}$ , again as predicted by the *trans* effect, yet curiously both 3G and 4-31G predict the S- $F_{ax}$  bond to be longer than S- $F_{eq}$ . The appreciable negative overlap populations between atoms *cis* to each other can be viewed as the molecular orbital counterpart of the concept of non-bonded steric repulsions, which has had remarkable success in rationalizing many aspects of molecular structure [19, 20]. In all cases *cis* Cl...F interactions have more negative overlap populations than do *cis* F...F, and it has already been argued that the shape of SF<sub>5</sub>Cl is governed by steric considerations [18]. Although the S-F distance in SF<sub>6</sub> [12] is known to be slightly less than the mean S-F distance in SF<sub>5</sub>Cl, only the 4-31G basis set gave a higher S-F overlap population in SF<sub>6</sub> than in SF<sub>5</sub>Cl. Basis set 4-31G predicts F in SF<sub>6</sub> to be less negative than in SF<sub>5</sub>Cl, whereas both 3G and 3G\* predict the reverse.

It was hoped originally that comparison of molecular orbital calculations at the minimum energy geometry with those performed at a standard reference structure would permit elucidation of the causes of the deviations away from that idealized geometry. Unfortunately this hope was not realized. While the total energy differences between reference and final geometries were relatively small, no more than 0.0015 hartree, changes in individual orbital energies were much larger than this, and the change in nuclear repulsion contributed as much as 0.1 hartree, so no dominant factor was apparent.

Earlier molecular orbital studies of SF<sub>5</sub>Cl [21] at the CNDO/2 level predicted the S- $F_{ax}$  bond to be shorter than S- $F_{eq}$ , and the Cl-S- $F_{eq}$  angle to be less than 90°. As is found for all three basis sets used in this work, the suggested dependence of  $\Delta r[(S-F_{ax}) - (S-F_{eq})]$  upon bond angle matches the predictions of VSEPR theory [2]. A series of CNDO calculations on TeF<sub>5</sub>X derivatives has been performed [22], at assumed geometries; in TeF<sub>5</sub>Cl the Te- $F_{ax}$  bond was predicted to be shorter than Te- $F_{eq}$ , and this finding used to rationalize the observed substitution pattern [23] of TeF<sub>5</sub>X compounds, in which F *cis* to X is replaced more readily than F *trans* to X, although it is not clear in such cases whether kinetic or thermodynamic factors are of greater importance. Moreover, it is now evident that the structural characteristics of such compounds are too subtle to be deduced reliably from rough, semiempirical calculations. Not even *ab initio* calculations of fair quality are adequate.

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