

Contribution from the Department of Chemistry,
University of Michigan, Ann Arbor, Michigan 48109**Structures of Hexacoordinate Compounds of Main-Group Elements.****1. A Combined Electron Diffraction–Microwave Study of SF₅Cl**

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In order to find whether fluorine bond lengths in SF₅Cl are in accord with the "primary effect" predicted by VSEPR theory ($r_{\text{eq}} > r_{\text{ax}}$) or whether, instead, they resemble those in IOF₅ where a "secondary effect" prevails ($r_{\text{ax}} > r_{\text{eq}}$), a structural study was carried out combining electron diffraction and published microwave spectroscopic data. A harmonic force field, constructed to reproduce all observed vibrational frequencies to within 2 cm⁻¹, was used in conjunction with Morse anharmonicity to convert diffraction and spectroscopic internuclear distance information to a common basis (r_z). Structural parameters, with estimated limits of error, were found to be $r_g(\text{S-Cl}) = 2.047$ (3) Å, $r_g(\text{S-F})_{\text{mean}} = 1.570$ (1) Å, $r_g(\text{S-F}_{\text{ax}}) - r_g(\text{S-F}_{\text{eq}}) = 0.022$ (10) Å, $r_g(\text{S-F}_{\text{eq}}) = 1.566$ (3) Å, $r_g(\text{S-F}_{\text{ax}}) = 1.588$ (9) Å, and $\angle\text{Cl-S-F}_{\text{eq}} = 90.7$ (0.2)°. Amplitudes of vibration determined from the diffraction data agreed well with those calculated from the force field. An excellent fit was achieved of calculated to observed average moments of inertia. It was observed that the small changes in r_z bond lengths caused by isotopic substitution were of great importance in the structure analysis. The experimental findings are discussed in the light of predictions of VSEPR theory and results of semiempirical molecular orbital calculations.

Introduction

Almost nothing is known about the systematics of molecular structures of hexacoordinate compounds AX₅Y of main-group elements. The reasons for this are simple. Such hypervalent compounds are most readily prepared if X is very electro-negative and most known representatives are fluorides. Since fluorine has only one stable isotope, AF₅Y molecules defy a complete structure analysis by microwave spectroscopy. Since there are only subtle differences between the two kinds of AF bonds in the molecule, a definitive resolution of the structure by electron diffraction is difficult. A recent study of vapor-phase IOF₅¹ confirmed, however, that, while microwave and electron diffraction data are individually inadequate for an unequivocal analysis of AX₅Y molecules, they lead to a unique and well-determined structure when combined. In the particular case of IOF₅ the following somewhat curious result was found: what is naturally interpretable as a "secondary relaxation effect" on the ($\text{IF}_{\text{ax}} - \text{IF}_{\text{eq}}$) bond length difference overrides and reverses the "primary effect". To find whether an analogous situation occurs in AX₅Y molecules when the difference between X and Y ligands is less extreme, we decided to investigate the molecule SF₅Cl for which microwave rotational constants of four isotopic species were already available.²

Experimental Section

The sample of SF₅Cl was purchased from PCR Inc. Initial analysis of its infrared spectrum showed SOF₂ to be present in small amounts. No impurities could be detected in that fraction of the sample consistently retained by a trap maintained at -112 °C. At -45 °C, the vapor pressure was measured as 239 Torr (lit.³ vapor pressure 235 Torr), and the gas-phase molecular weight was found to be 163 (calculated mol wt 162.5).

Diffraction patterns were recorded on 4 × 5 in. Kodak electron image plates using the electron diffraction unit at the University of Michigan,⁴ with an r^3 sector, at nozzle to plate distances of 21, 11, and 7 cm. Forty-kilovolt incident electrons were employed. Full experimental conditions are given in Table I.

Plates were developed at 20 °C for 3 min with Kodak HRP developer to which antifog solution had been added. An automated recording microphotometer, with digital output, measured the absorbance at 1/8-mm intervals, while the plates were spun about the center of the diffraction pattern. Absorbances were converted to exposures by the relationship⁵

$$E = A(1 + 0.116A + 0.0179A^2 + 0.00312A^3)$$

where E and A are respectively the exposure and absorbance.

Analysis of Data

Experimental intensities were obtained by averaging the data from five plates selected for each camera distance. After corrections were

Table I. Experimental Conditions for Recording Electron Diffraction Patterns of SF₅Cl

	Camera distance, cm		
	21.075	11.067	6.430
Nozzle temp, °C	27	27	27
Reservoir temp, °C	-85	-85	-85
Vapor pressure, Torr	20	20	20
Exposure time, s	7-9	10-12	30-40
Beam current, μA	0.44	0.79	0.79
Diameter of Pt nozzle, mm	0.25	0.25	0.25
Nozzle to beam distance, mm	0.46	0.46	0.46

applied for extraneous scattering and for irregularities in the sector opening, the intensities were leveled. For sulfur and chlorine, the elastic and inelastic scattering factors of Schafer, Yates, and Bonham⁶ were used, but those for fluorine were taken from the data reported by Cox and Bonham.⁷ Molecular parameters were refined by a least-squares process, which imposed geometrical self-consistency on the internuclear distances, comparing experimental and calculated values of the reduced molecular intensity $M(s)$. Intensity data for the three camera distances were initially treated separately. Diagonal weight matrices were used, with elements proportional to the scattering variable s , but the uncertainties were augmented to account for correlation ($\gamma \approx 1$ Å)⁴ between neighboring data points. Once the individual background functions had been established, the three data sets were blended together. The indices of resolution were 0.85, 0.86, and 0.81 for the 21-, 11-, and 7-cm camera distances, respectively. At this stage it became apparent that the 21-cm data were not quite consistent with the other two sets. Although no evidence of impurities could be found, a nonrandom error signal was visible in the $M(s)$ residuals. Rather than run the risk of introducing systematic errors, we felt it best to discard the 21-cm data. Low-angle scattering data are not particularly important for determining the structure of SF₅Cl as there are no long internuclear distances or large amplitudes of vibration. The 11- and 7-cm data were interpolated in units of $\Delta s = \pi/10$, covering the range $9.4 \leq s \leq 57.2$. Radial distribution functions were calculated using a damping factor of $\exp(-0.0015s^2)$. Anharmonicity constants⁸ were taken to be 1.8 Å⁻¹ for S-F bonds,^{9,10} 1.6 Å⁻¹ for S-Cl bonds, and 1.5 Å⁻¹ for all nonbonded distances. Approximate shrinkage corrections for the nonbonded distances were calculated from the harmonic force field discussed below.

Conversion to Average Structure

Electron diffraction and microwave spectroscopy supply different types of structural information. For cases such as the present one where neither technique can unambiguously determine all parameters with high precision, it is beneficial to combine data from both experiments, provided that proper account is taken of the different definitions of bond length and the different vibrational averaging involved. Electron diffraction studies generally report r_g distances, whereas r_0 or r_s parameters are obtained from microwave spectroscopy. In order to convert these different types of parameters to a common basis, a knowledge of the molecular force field is necessary.

Table II. Observed and Calculated Vibrational Spectra and Force Field

Normal mode	Symmetry class	Approx description	Freq, cm ⁻¹	
			Obsd	Calcd
1	a ₁	S-F axial str	854.6	857
2		SF ₄ equatorial square str	707.1	708
3		SF ₄ out-of-plane def	601.9	602
4		S-Cl str	401.7	402
5	b ₁	SF ₄ equatorial square str	625	625
6		SF ₄ out-of-plane def	N.o.	317
7	b ₂	SF ₄ in-plane def	505	506
8	e	SF ₄ equatorial square str	909.0	909
9		SF ₄ wag	579.0	579
10		SF ₄ in-plane def	441.0	441
11		SF ₅ rock	271	271

Force Field

$$\begin{aligned}
 k_r &= 4.65, k_R = 4.64, k_D = 2.76 \text{ mdyn/\AA} \\
 k_{rr} &= 0.27, k_{rr'} = 0.26, k_{rR} = 0.27, k_{Dr} = 0.18, k_{DR} = 0.23 \text{ mdyn/\AA} \\
 k_\alpha &= 2.11, k_\beta = 2.11, k_\gamma = 1.74 \text{ mdyn \AA/rad}^2 \\
 k_{r\alpha} &= 0.55, k_{r\beta} = 0.55, k_{r\gamma} = 0.40, k_{R\beta} = 0.55, k_{D\gamma} = 0.37 \text{ mdyn/rad} \\
 k_{\alpha\alpha'} &= 0.20, k_{\alpha\beta} = 0.28, k_{\alpha\gamma} = 0.24, k_{\beta\beta} = 0.28, k_{\alpha\alpha''} = 0.05 \text{ mdyn \AA/rad}^2 \\
 k_{\beta\beta'} &= 0.20, k_{\beta\gamma} = 0.13, k_{\gamma\gamma} = 0.26, k_{\gamma\gamma'} = 0.05 \text{ mdyn \AA/rad}^2
 \end{aligned}$$

The vibrational spectra of SF₅Cl have been recorded and are not in doubt, but three conflicting assignments may be found in the literature.^{3,11,12} It appeared to us that the third of these, due to Christe et al.,¹² was the most reasonable. Initial values of the valence force constants were taken from those reported for SF₆,¹³⁻¹⁵ which are well determined due to the high symmetry, the available frequency shifts for ³⁴SF₆, and the Coriolis coupling constants. They were altered empirically so as to reproduce the observed frequencies to within 2 cm⁻¹. The final force constants used, together with the experimental and calculated vibrational frequencies, are listed in Table II. There are 39 terms in the general valence force field for SF₅Cl but only 10 observed frequencies. Some simplification was achieved by assuming that all interactions of the type $r\alpha$ were zero, unless the bond r was one of the two defining the angle α . Twenty-six force constants remain, namely, $k_r, k_R, k_D, k_\alpha, k_\beta, k_\gamma, k_{rr}, k_{rr'}, k_{rR}, k_{rD}, k_{RD}, k_{r\alpha}, k_{r\beta}, k_{r\gamma}, k_{R\beta}, k_{D\gamma}, k_{\alpha\alpha'}, k_{\alpha\beta}, k_{\alpha\gamma}, k_{\beta\beta}, k_{\beta\gamma}, k_{\gamma\gamma}, k_{\beta\beta'}, k_{\gamma\gamma'}, k_{\beta\beta''}, k_{\gamma\gamma''}$, where r represents the equatorial S-F distances, R the axial S-F distance, and D the S-Cl bond. Bond angles α, β , and γ represent F_{eq}-S-F_{eq}, F_{eq}-S-F_{ax}, and F_{eq}-S-Cl, respectively. In bond-bond couplings, rr refers to two adjacent r , and rr' to two opposite r . In angle interactions, $\alpha\beta$ implies α and β share a common bond and that the other two bonds are perpendicular; $\alpha\alpha'$ implies that α_1 and α_2 share a common bond and that the other two bonds are parallel; $\alpha\alpha''$ implies that each bond defining α_1 is parallel to a bond defining α_2 . Finally, $r\alpha$ implies that r is one of the bonds defining α . Since the two bond lengths r and R are very similar and all angles are close to 90°, it is reasonable to assume that many of these terms must be almost identical, if not exactly equal. To obtain an approximate fit to the frequencies and rough values for the force constants, we assumed initially that $k_r = k_R, k_{rr} = k_{rR}, k_\alpha = k_\beta, k_{r\alpha} = k_{r\beta} = k_{R\beta}, k_{\alpha\beta} = k_{\beta\beta}$, and $k_{\alpha\alpha'} = k_{\beta\beta'}$ and that the ratios of k_{rD} to k_{rr}, k_{RD} to $k_{rr'}, k_{r\gamma}$ to $k_{r\alpha}, k_{\gamma\gamma}$ to $k_{\alpha\beta}$, and $k_{\gamma\gamma'}$ to $k_{\beta\beta'}$ were roughly equal to the ratio of k_γ to k_α . Final force constants were obtained by relaxing some of these constraints slightly to achieve a better frequency fit, but no gross departures from these rules were necessary, nor is any parameter very different from the analogous value in SF₆. Our force field predicted a frequency separation between the ν_4 S-³⁵Cl and S-³⁷Cl stretching vibrations of 8 cm⁻¹, whereas if the assignment of Christe et al. is assumed, the observed shift is 6 cm⁻¹.³ It is not clear how much uncertainty there is in this measurement, as the sloping background due to the main S-³⁵Cl peak appears to displace the maximum of the S-³⁷Cl peak to higher frequency. Using constraints on the force field similar to

Table III. Reductions in r_z Bond Lengths, Compared to ³²SF₅³⁵Cl, Caused by Isotopic Substitution (Units Å)

	³⁴ SF ₅ ³⁵ Cl	³² SF ₅ ³⁷ Cl	³⁴ SF ₅ ³⁷ Cl
$r(\text{S-Cl})$	0.000 04	0.000 05	0.000 08
$r(\text{S-F}_{\text{eq}})$	0.000 04	0.0	0.000 04
$r(\text{S-F}_{\text{ax}})$	0.000 04	0.000 01	0.000 05

those outlined above, we were unable to find a set of force constants to reproduce the frequencies of either of the other two vibrational assignments, and we suggest that this observation reinforces other evidence¹² that the assignment of Christe et al. is the correct one. After this work was completed, another study of the force field of SF₅Cl was published.¹⁶ Although somewhat different constraints were imposed, the force constants obtained are mostly very similar to those reported here.

The procedure for simultaneous least-squares analysis of electron diffraction intensities and moments of inertia derived from spectroscopy was similar to that devised by Kuchitsu et al.¹⁷ The r_g internuclear distances obtained from electron diffraction were converted to r_α° parameters using the expression¹⁸

$$r_\alpha^\circ = r_g - \delta r_{\text{cent}} - \frac{3}{2}a(l_T^2 - l_0^2) - K_0$$

in which δr_{cent} is the centrifugal distortion due to the rotational motion of the molecule, a is the Morse anharmonicity constant,⁸ l^2 is the mean-square amplitude of vibration at temperature T or zero, and K_0 is a correction due to the zero-point perpendicular amplitudes of vibration for the distance concerned.

The B_0 effective rotational constants, obtained from the microwave study, were converted to the zero-point average constants B_z using the relationship

$$B_z = B_0 + \Delta B_{\text{vib}}$$

in which the vibrational correction ΔB_{vib} was calculated by the program MSAV, written by R. L. Hilderbrandt.

Particular attention was paid to the small changes in r_z bond lengths caused by isotopic substitution, which have been shown to be important in earlier work.¹⁹ Bond lengths, r_z , refer to the molecule in the ground vibrational state; since vibrations are in general anharmonic, the distance between mean positions changes slightly if the nuclear masses are changed but the force constants remain unaltered. The δr_z terms were calculated by the approximate expression

$$\delta r_z = \frac{3a}{2}(l_{ij}^2 - l_{ik}^2)_{T=0} - (K_{ij} - K_{ik})_{T=0}$$

where l_{ij} and l_{ik} refer to the isotopic species ij and ik , a, l , and K having the same meaning as above. The values calculated for δr_z for the three substituted isotopic species are listed in Table III.

We attempted to give least-squares weights to the diffraction data points and to the corrected moments of inertia appropriate to their uncertainties. The original measurements of B_0^2 are beautifully precise, but uncertainties are introduced by the ΔB_{vib} correction term. We assumed that the uncertainty in the term was 10% of its value, giving a precision of 1 part in 20 000 for B_z . Since the standard deviation of the fit of the electron diffraction data points was rather less than 1 ppt, the corrected moments of inertia were assigned weights of 250, on a scale where the highest weighted diffraction point had unit weight.

Results

From Electron Diffraction Alone. The experimental and final calculated molecular intensity curves are shown in Figure 1, and the radial distribution function is shown in Figure 2. SF₅Cl is known from the microwave studies to have C_{4v} symmetry,² so only four geometrical parameters are required to define the structure. We chose these to be the S-Cl bond length, the mean S-F bond length, the difference Δr between the S-F_{ax} and S-F_{eq} bond lengths, and the Cl-S-F_{eq} angle. Our results are presented in Table IV. The agreement between observed and calculated amplitudes of vibration is satisfactory.

Five distinct peaks, one of which has an evident shoulder, are seen in the radial distribution function. They may be readily assigned as illustrated in Figure 2. It might be thought

Table IV. Structural Parameters for SF₅Cl^a

		ED ^b I	ED ^c II	ED + MW ^d III	$r_g - r_z^e$	Shrinkage ^e	Calcd amplitude of vib ^e
$r(\text{S-Cl})$	r_1	2.052 (4)	2.049	2.045 (3)	0.0024		
$r(\text{S-F})_{\text{mean}}$	r_2	1.569 (2)	1.567	1.568 (1)			
$r(\text{S-F}_{\text{ax}}) - r(\text{S-F}_{\text{eq}})$	r_3	-0.003 (20)		0.022 (10)			
$r(\text{S-F}_{\text{ax}})$		1.567 (14)	1.565	1.586 (9)	0.0020		
$r(\text{S-F}_{\text{eq}})$		1.570 (4)	1.568	1.564 (3)	0.0019		
$\angle \text{Cl-S-F}_{\text{eq}}$	L	90.6 (0.3)		90.73 (0.2)			
$r(\text{Cl} \cdots \text{F}_{\text{eq}})$		2.597 (4)		2.590 (3)	0.0048	0.0006	
$r(\text{Cl} \cdots \text{F}_{\text{ax}})$		3.616 (15)		3.630 (12)	0.0025	0.0028	
$r(\text{F}_{\text{eq}} \cdots \text{F}_{\text{eq}})_{\text{cis}}$		2.220 (5)		2.211 (4)	0.0033	0.0005	
$r(\text{F}_{\text{ax}} \cdots \text{F}_{\text{eq}})$		2.205 (6)		2.213 (6)	0.0035	0.0004	
$r(\text{F}_{\text{eq}} \cdots \text{F}_{\text{eq}})_{\text{trans}}$		3.137 (8)		3.127 (6)	0.0017	0.0027	
$l(\text{S-F}_{\text{eq}})^f$	l_1	0.044 (2)		0.044 (2)			0.043
$l(\text{S-F}_{\text{ax}})^f$		0.044					0.043
$l(\text{S-Cl})$	l_2	0.050 (4)		0.051 (4)			0.048
$l(\text{Cl} \cdots \text{F}_{\text{eq}})$	l_3	0.067 (3)		0.068 (3)			0.070
$l(\text{Cl} \cdots \text{F}_{\text{ax}})$	l_4	0.062 (12)		0.064 (14)			0.057
$l(\text{F}_{\text{eq}} \cdots \text{F}_{\text{eq}})_{\text{cis}}$	l_5	0.060 (3)		0.061 (3)			0.063
$l(\text{F}_{\text{ax}} \cdots \text{F}_{\text{eq}})^g$		0.060					0.063
$l(\text{F}_{\text{eq}} \cdots \text{F}_{\text{eq}})_{\text{trans}}$	l_6	0.057 (8)		0.058 (8)			0.054
$[\sigma(I)]/I^h$		6.5×10^{-4}		8.0×10^{-4}			
$[\sigma(I_B^z)/I_B^z]^i$		1.8×10^{-3}		4.9×10^{-7}			

^a ED = electron diffraction; MW = microwave. Units are Å for distances, shrinkages, and amplitudes of vibration and are degrees for the angle. The last two entries are dimensionless. ^b r_g distances, l_g amplitudes; uncertainties are 2.5σ , where σ includes random errors, estimates of possible systematic errors, and effects of correlation between neighboring data points ($\gamma \approx 1$ Å). ^c r_z distances, l_z amplitudes; uncertainties are intended to be limits of error. ^e Calculated from harmonic force field given in Table II, using program MSAV. ^f Constrained to be 0.000 15 Å greater than l_1 , as indicated by force field calculations. ^g Constrained to be 0.000 38 Å greater than l_2 , as indicated by force field calculations. ^h Fractional weighted standard deviation of electron diffraction intensities. ⁱ Fractional weighted standard deviation of average moments of inertia.

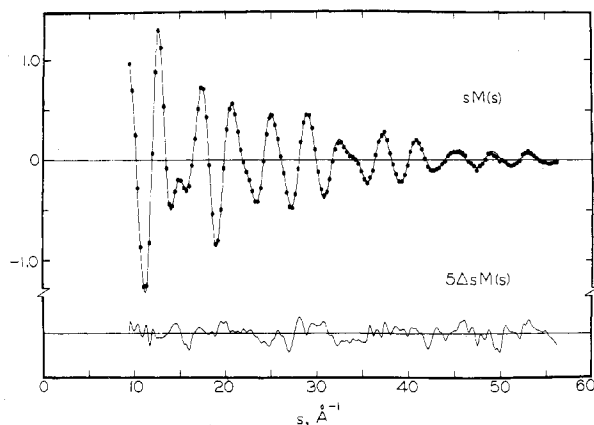


Figure 1. Experimental and calculated molecular intensity functions for SF₅Cl: solid circles, experimental points; smooth line, theoretical curve. $\Delta sM(s) = sM(s)_{\text{exptl}} - sM(s)_{\text{calcd}}$.

that all four parameters could be determined with high precision from the position of five peaks in the radial distribution function, but this is not the case. The diffracted intensity is not equally sensitive to small changes in each of the geometrical parameters. For only two of the peaks, those at 3.14 and 3.62 Å, is the derivative of the position with respect to the bond length split Δr greater than 0.1, being 0.4 and 0.8 for those two distances. Since these two distances represent but a small fraction of the total molecular scattering, the difference in S-F bond lengths is relatively poorly determined by the diffraction data. Inspection of Table IV shows its uncertainty to be several times greater than those of the S-Cl distance or the mean S-F distance.

From Combined Analysis of Diffraction and Spectroscopic Data. The results obtained from the combined analysis are given in Table IV. It can be seen that the difference in S-F bond lengths is the only parameter whose value is appreciably different from that found in the analysis based on diffraction data alone. We feel that the results from the combined

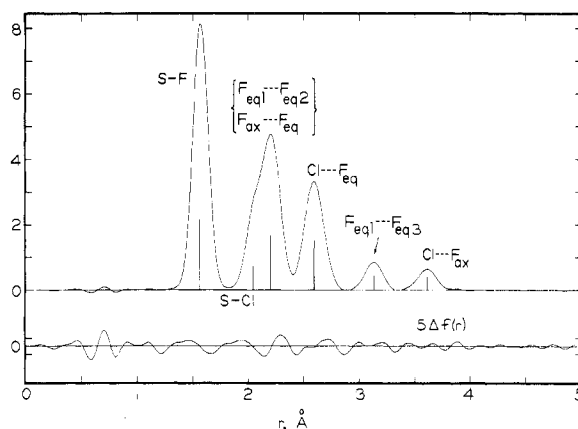


Figure 2. Experimental radial distribution function for SF₅Cl. $\Delta f(r) = f(r)_{\text{exptl}} - f(r)_{\text{calcd}}$.

analysis are the more reliable and are to be preferred. The inclusions of the four rotational constants has reduced the least-squares estimates of the standard deviations of the S-F bond length split Δr , the Cl-S-F_{eq} angle, and the S-Cl bond length by factors ranging from 3.5 to 12, while scarcely changing the standard deviation of the mean S-F bond length. Furthermore, it is known that electron diffraction is a relatively poor method for determining small differences between similar but non-symmetry-related distances between identical pairs of atoms, the calculated difference being correlated with certain systematic errors in intensity measurements, so it is probable that the uncertainty listed for the bond length split in column 1 of Table IV is unrealistically small. It was observed that changing the relative weights of spectroscopic and diffraction data from 250:1 either to 5:1 or to 10⁷:1 led to only trivial changes in the calculated parameters, changes insignificant compared to other uncertainties involved. It was found that the best fit of the calculated to observed corrected moments of inertia was obtained if the datum for ³⁴SF₅³⁷Cl was weighted down to 10, relative to the weights of the data

Table V. Experimental Rotational Constants, Vibrational Corrections, and Comparison of Experimental and Calculated Average Moments of Inertia for SF₅Cl Isotopic Species

	³² SF ₅ ³⁵ Cl	³⁴ SF ₅ ³⁵ Cl	³² SF ₅ ³⁷ Cl	³⁴ SF ₅ ³⁷ Cl
Exptl rotational const, MHz	1824.560 (5)	1823.857 (5)	1783.524 (5)	1782.70 (3)
$B_0 - B_z$, MHz	0.905	0.904	0.878	0.878
Av moment of inertia, I_B^z , amu Å ²	277.1243 (8)	277.2310 (8)	283.4994 (8)	283.6305 (45)
Calcd moment of inertia, amu Å ²	277.1242	277.2311	283.4995	283.6296
Δ , amu Å ²	0.0001	-0.0001	-0.0001	0.0009

Table VI. Matrix of Correlation Coefficients for SF₅Cl: ED Analysis^a

	r_1	r_2	r_3	L	l_1	l_2	l_3	l_4	l_5	l_6	R
σ	0.0011	0.000 20	0.0044	0.068	0.000 33	0.000 93	0.000 77	0.0035	0.000 55	0.0023	0.0055
r_1	100	-25	-18	-74	-4	<1	<1	<1	-2	-5	3
r_2		100	4	24	6	7	-4	1	10	2	10
r_3			100	54	20	<1	11	-2	25	3	9
L				100	-5	-7	-5	-5	2	4	-24
l_1					100	19	29	5	35	6	69
l_2						100	8	3	41	2	29
l_3							100	2	14	<1	41
l_4								100	4	-4	8
l_5									100	5	47
l_6										100	7
R											100

^a Matrix elements given by $\rho_{ij} = (M_x)_{ij} / [(M_x)_{ii}(M_x)_{jj}]^{1/2}$, where M_x is the zeroth-order error matrix.⁴ Only the upper half of the matrix is given. All entries, except for the standard deviations, have been multiplied by 100. The numbering of the parameters follows from Table IV. Units for σ are Å for bond lengths and amplitudes of vibration and degrees for the angle. R is dimensionless.

for other isotopic species of 250. This observation is consistent with the greater experimental uncertainty in the B_0 measurement for ³⁴SF₅³⁷Cl, caused by its low natural abundance, although the presumed uncertainty in ΔB_{vib} is still greater than that in B_0 . Some authors have argued¹⁹ that the moment of inertia for the parent isotopic species, in this case ³²SF₅³⁵Cl, should be assigned a higher weight than those for the substituted species, since for the parent there is no uncertainty introduced by the small changes in r_z bond lengths caused by isotopic substitution. When this procedure was followed, the resulting parameters were insignificantly different from those listed in Table IV.

It is pleasing that the average moments of inertia are reproduced very well by the structure given in Table IV. In Table V are presented the original B_0 measurements, the vibrational corrections applied to give B_z parameters, the resulting average moments of inertia, and the calculated moments. The uncertainties listed for I_B^z are derived solely from those in the B_0 measurements and include no provision for possible errors in the $B_0 \rightarrow B_z$ conversion. For all four isotopic species the difference between the calculated and corrected moments is much less than the quoted uncertainty in the B_0 measurements,² although unfortunately it was not made clear whether the uncertainties quoted are standard deviations, limits of error, or some other quantity.

The correlation matrix derived from the analysis based on diffraction data alone is given in Table VI. There are no intolerably large elements. No information about the amplitudes of vibration can be deduced from the spectroscopic moments. Accordingly only those elements referring to the geometrical parameters are given in the correlation matrix derived from the combined analysis, listed in Table VII. Contrary to first intuitive expectations, the correlation between the geometrical parameters is increased by the addition of spectroscopic data. Since four moments of inertia are available, which depend upon four geometrical parameters, the addition of those four moments to a data set of 150 members as extra observations of high weight increases the correlation between the parameters. This is not serious, so

Table VII. Matrix of Correlation Coefficients for SF₅Cl: ED + MW Analysis^a

	r_1	r_2	r_3	L
σ	0.000 14	0.000 22	0.0016	0.011
r_1	100	-7	-17	-51
r_2		100	-97	88
r_3			100	-75
L				100

^a Numbering and units of parameters as in Table VI.

long as the moments of inertia themselves are not correlated. More significant is the fact that the standard deviations drop appreciably.

The uncertainties listed in column 3 of Table IV are intended to represent limits of error and for geometrical parameters are greatly increased from the least-squares estimates given in Table VII. In order to assess realistic values for these limits, we observed the effects of simulating various systematic errors. The S-Cl bond length was found to be the parameter most effected by small changes in the original B_0 measurements (or in the B_0 to B_z correction terms). This behavior is expected, since the microwave data determine the S-Cl bond length uniquely but do not provide unambiguous values of the other parameters.

We found that the small quantities δr_z (the changes in average bond length brought about by isotopic substitution) were the correction terms with the greatest influence on the molecular parameters. Changing δr_z for the S-Cl distance for one isotopic species by only 10^{-5} Å led to a change in the calculated bond length of 0.0014 Å, or 10 apparent standard deviations. If the δr_z terms were omitted entirely, the fractional weighted standard deviation of the electron diffraction intensities increased by 70%, and the standard deviation of the fit of the moments of inertia increased by 280%. The S-Cl bond length decreased by 0.014 Å, or nearly 40σ , to 2.031 Å, while the S-F bond length difference increased to 0.048 Å, a change of 10σ . The r_3 value for the S-Cl bond length is 2.030 Å,² appreciably smaller than the r_z value of 2.045 Å. If the small decreases in bond length caused by the substitution

of heavier isotopes are neglected, the r_s coordinates calculated are smaller than mean coordinates, although r_s bond lengths may be either larger than or smaller than mean bond lengths, depending upon the position of the atoms with respect to the center of mass.²⁰ This effect is particularly important for atoms close to the center of mass; in the present case the S coordinate is 0.18 Å.

There are two disturbing features of this work which lead us to suspect the presence of some small systematic errors. The first is that the fit of the diffraction intensity data worsened appreciably when the microwave data were added. We do not think that this is due to a scale error in the diffraction experiment, since, if the data were scaled so that the structure derived from the diffraction data reproduced the moments of inertia as well as possible, the fit of the diffraction intensities worsened when the microwave moments of inertia were added to the analysis by almost as much as they did originally. The second is that the values derived for the geometrical parameters varied according to which isotopic species were included in the analysis. The spread in values was on occasion several times greater than the apparent standard deviation. It is this factor above all which led us to adopt the conservative limits of error listed in Table IV.

It will be noted that in order to correct electron diffraction r_g distances into r_{α}° parameters, the appropriate Morse anharmonicity must be used. While this can be estimated satisfactorily for bonded distances, very little information is available for nonbonded distances. We followed two different approaches for the nonbonded $r_g \rightarrow r_{\alpha}^{\circ}$ conversions. First we assumed a Morse anharmonicity of 1.5 for all nonbonded distances. Second, we determined what change in nonbonded distances resulted by resolving the $r_g - r_{\alpha}^{\circ}$ terms from the two constituent bonded distances along the nonbonded direction. The differences between the geometrical parameters resulting from these two approaches were much smaller than the uncertainties listed in Table IV.

Discussion of Structure

We have shown that in SF₅Cl the S-F_{ax} distance is slightly greater than the S-F_{eq} distance and that the Cl-S-F_{eq} angle is slightly greater than 90°. It is of interest to compare these findings with the predictions of the widely successful VSEPR theory.²¹ The replacement of an F atom in SF₆ by the less electronegative Cl atom causes the bonding electron pair involved to move "closer" to the central S atom, in the language of VSEPR theory. As it moves closer to the equatorial bonding pairs, the resulting increased "repulsion" is expected to lengthen the equatorial bonds and increase the Cl-S-F_{eq} angle to greater than 90°. Such a response might be envisioned as a "primary effect" of chlorine substitution. However, if the Cl-S-F_{eq} angle were increased substantially, the equatorial bonding pairs would encroach upon the space occupied by the S-F_{ax} bonding pair, and the S-F_{ax} bond would thus be lengthened by the extra repulsion in what may be viewed as a "secondary relaxation" effect. Since it is not clear by how much the Cl-S-F_{eq} angle must be increased before the inversion in the pattern of bond lengthening occurs, it can fairly be said that the predictions of VSEPR theory for this molecule are equivocal. A more complete discussion of the VSEPR interpretation will be published elsewhere.

Our experimental results received some support from semiempirical molecular orbital calculations at the extended-Hückel level.²² VOIP for the 3s and 3p orbitals on S and Cl, together with those for the 2s and 2p orbitals on F, were taken from the work of Basch, Viste, and Gray²³ and were adjusted to be self-consistent with the calculated net atomic charges. Exponents for these orbitals were taken from Clementi and Raimondi.²⁴ 3d orbitals, when included on either S or Cl, were assigned VOIP or 6 eV and exponents of 1.1.

The S-F_{eq} and S-F_{ax} bond lengths were taken to be identical, to eliminate any variation in overlap with distance.

With bond angles fixed at 90°, the calculated S-F_{ax} bond overlap population was lower than for S-F_{eq}, whether or not d orbitals were included. As the Cl-S-F_{eq} angle was increased, the difference in bond overlap populations increased and the molecular energy became more negative. At the experimental bond angle of 90.7°, the difference in populations was consistent with a bond length difference of roughly 0.01–0.02 Å.²⁵ The mean S-F bond population was lower than that found in parallel calculations on SF₆. This is consistent with current work in our laboratory,²⁶ in which preliminary analyses show that the r_g S-F bond length in SF₆ is 1.561 Å, or 0.009 Å shorter than the mean length in SF₅Cl. When d orbitals were included on S, the calculated S-F bond populations increased, due to overlap between the p_{π} orbitals on F and the d orbitals on S. The effect of including d orbitals on Cl, however, was to weaken the S-Cl bond and strengthen the S-F bonds. Such behavior has elsewhere been called "altruistic".²⁷ The calculated net atomic charges at the experimental Cl-S-F_{eq} angle were as follows: S +0.70 (+1.14), Cl +0.13 (-0.03), F_{ax} -0.18 (-0.23), and F_{eq} -0.16 (-0.22) with (without) 3d orbitals on S and Cl.

Earlier molecular orbital studies of SF₅Cl,²⁸ at the CNDO/2 level, predicted that the Cl-S-F_{eq} angle would be less than 90°, the value of 88° 50' resulting from energy minimization when axial and equatorial bond lengths were held equal, and that the S-F_{ax} bond would be shorter than the S-F_{eq} bonds. Although both predictions are contradicted by our experimental findings, the suggested dependence of Δr (ax-eq) upon the Cl-S-F_{eq} angle is in accord with VSEPR theory.

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Registry No. SF₅Cl, 13780-57-9; ³²SF₅³⁵Cl, 25478-94-8; ³⁴SF₅³⁵Cl, 60349-31-7; ³²SF₅³⁷Cl, 35167-17-0; ³⁴SF₅³⁷Cl, 60349-32-8.

Supplementary Material Available: Tables of the leveled intensities $I_0(s)$ and the background functions $I_B(s)$ for the 11- and 7-cm camera distances (7 pages). Ordering information is given on any current masthead page.

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Structures of Hexacoordinate Compounds of Main-Group Elements.

2. A Combined Electron Diffraction–Microwave Study of IOF₅

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The molecular geometry and mean amplitudes of vibration of vapor-phase IOF₅ were determined. Derived structural parameters ($\pm 2\sigma$) were $r_g(\text{IO}) = 1.715$ (4) Å, $r_g(\text{IF}_{\text{eq}}) = 1.817$ (2) Å, $r_g(\text{IF}_{\text{ax}}) = 1.863$ (4) Å, and $\angle \text{OIF}_{\text{eq}} = 98.0$ (3)°. The finding that the axial IF bond is longer than the equatorial IF bonds is contrary to the primary deformation expected according to several popular viewpoints. These include the effect of adjacent bonds in VSEPR theory and the trans effect inferred from overlap populations in molecular orbital treatments in which the isoelectronic molecule TeF₆ is perturbed by moving a proton from an axial ligand to the Te nucleus. More detailed molecular orbital analyses as well as a semiquantitative VSEPR (points-on-a-sphere) treatment revealed, however, that when bond angles were allowed to relax from their initial 90° values, the secondary relaxation effect upon the bond lengths reverses the axial and equatorial bond lengths. It appears for MX_nY_{6-n} compounds of main-group elements that such reversals may be quite general. Indeed, in the cases of MX₂Y₄ and MX₃Y₃, secondary relaxations from 90° structures may commonly reverse the stabilities of the two possible stereoisomers. On the other hand, in the competition between lone pairs X and bond pairs Y, the primary VSEPR effect seems to prevail. The underlying ideas are discussed briefly.

Introduction

The Gillespie–Nyholm valence shell–electron pair repulsion (VSEPR) theory^{2,3} for directed valence neatly rationalizes structural features of many hypervalent compounds of main-group elements. By postulating a plausible hierarchy of repulsive properties (space-filling requirements) of lone pairs and of bonds to ligands of varying degrees of electronegativity, the VSEPR theory systematizes effects which are sometimes referred to as the "mutual influence of ligands" including the "trans effect".⁴ Of particular concern in the present research are compounds that are hexacoordinate in fact or in the VSEPR sense by virtue of lone pairs on the central atom being considered to act as "ligands". The molecule IOF₅, whose structure has not been published heretofore, is closely analogous, according to the VSEPR point of view, to such molecules as XeOF₄, IF₅, and TeF₆. Now, the known structures of the last three molecules⁵⁻⁸ are satisfactorily accounted for by VSEPR theory. Therefore, it was of special interest to note in the case of IOF₅ that the VSEPR theory and simple molecular orbital arguments are equivocal and can lead quite naturally to incorrect predictions. These will be discussed in this paper in conjunction with a molecular structure determination of IOF₅ by gas-phase electron diffraction.

Previous spectroscopic investigations have established a C_{4v} point group symmetry for IOF₅⁹⁻¹² and suggested a nearly octahedral geometry.^{13,14} While insufficient to determine a complete structure for IOF₅, the rotational constants for the ¹⁶O and ¹⁸O species derived from the microwave investigation⁹ are valuable adjuncts to the electron diffraction data for the present analysis, as will be discussed.

Experimental Section

A sample of IOF₅ was prepared at Argonne National Laboratory. All surfaces contacting the reactive substance before its introduction into the electron beam of the diffraction apparatus were of seasoned nickel or Monel Metal. Diffraction patterns were recorded on 4 × 5 in. Kodak Process plates using an electron diffraction unit described elsewhere,¹⁵ employing 40-kV incident electrons with an r^3 sector at

camera distances of 21, 11, and 7 cm. Sample pressures were the vapor pressures at -45 °C (21-cm data) or -37 °C (11- and 7-cm data). Measurements of absorbances of the diffraction plates were carried out as the plates were spun about the pattern centers.

Analysis of Data

Experimental intensities were obtained by averaging the data from four plates selected for each camera distance. Scattering factors used both for leveling the data and for subsequent least-squares analyses were the elastic form factors of Cox and Bonham¹⁶ and the inelastic factors (for oxygen and fluorine) of Tavard¹⁷ and (for iodine) of Pohler and Hanson.¹⁸ Backgrounds and indices of resolution (1.04, 1.05, and 1.00 at the 21-, 11-, and 7-cm camera distances, respectively) were refined for the individual camera geometries separately. The resultant reduced molecular intensities, $M(s)$, were then merged to give a single set extending from $s = 5$ to $s = 45$ Å⁻¹, interpolated in units of $\Delta s = \pi/10$. The resultant curve is depicted in Figure 1. Experimental leveled intensities and backgrounds are available as supplementary material. Initial structure refinements were performed upon radial distribution functions calculated with a damping factor of $\exp(-0.00125s^2)$. Final refinements were carried out upon the leveled intensities.¹⁵ Asymmetry constants a were estimated¹⁹ to be 2.3 Å⁻¹ for the I–O bonded distance and 2.1 Å⁻¹ for the I–F distances and were taken to be 2.0 Å⁻¹ for all nonbonded distances. No account was taken of dynamic scattering effects beyond those implicit in the partial wave atomic scattering factors.¹⁶ Corrections for the Bastiansen–Morino shrinkage effect²⁰ were based on calculated shrinkages for the isoelectronic molecule TeF₆.²¹ These estimated shrinkages, 0.0006 Å for O...F_{eq}, 0.0010 Å for F_{eq}...F_{eq}(short), 0.0008 Å for F_{eq}...F_{ax}, 0.0045 Å for F_{eq}...F_{eq}(long), and 0.0040 Å for the O...F_{ax} distances, differ insignificantly from those calculated from spectroscopic data for IOF₅ itself.^{22,23}

Although the imposition of geometrical self-consistency on the set of internuclear distances for IOF₅ reduces to 4 the number of independent geometrical parameters, additional