

STRUCTURES OF HEXACOORDINATE COMPOUNDS OF MAIN-GROUP ELEMENTS

Part III. An electron diffraction study of SF₆

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ABSTRACT

Gas-phase sulphur hexafluoride is a regular octahedron with an S—F bond length (r_g) of 1.561(2) Å and mean amplitudes of vibration of 0.044(1) Å for S—F, 0.056(6) Å for F—F_{trans}, and 0.061(2) Å for F—F_{cis}. Uncertainties correspond to 3σ .

INTRODUCTION

In the course of an investigation of the structure of SF₅Cl [1], it was found that only incomplete structural information exists for SF₆, the most natural reference compound for sulfur(VI)—fluorine bond lengths and a molecule under intense investigation in research on laser-induced processes [2]. Spectroscopic analyses have confirmed that the molecule possesses O_h symmetry [3] but the published diffraction studies are uncertain by about 0.02 Å [4—6]. It seemed worthwhile to test predictions of the VSEPR [7] theory concerning the S—F bond lengths in SF₅Cl versus the length in SF₆. Therefore, we undertook a study of SF₆ by vapor-phase electron diffraction.

EXPERIMENTAL

The sample of SF₆ with a stated purity of 99.99% was purchased from M. G. Scientific Co. IR spectra and vapor phase chromatograms revealed no contaminants. Mass spectrographic analyses indicated the presence of only minor concentrations of impurities. Electron diffraction patterns of a solid sample maintained at -106°C were recorded on 4×5 in. Kodak Electron Image plates. Experimental conditions (see Table 1)* and analyses of data closely resemble those reported for SF₅Cl [1]. O_h symmetry was assumed in least squares refinements and asymmetry constants, a , were taken as 1.8 \AA^{-1} for all internuclear distances. The shrinkage values of

*Tabulated levelled intensities $I_0(s)$ and background functions $I_B(s)$ for 21—, 11—, and 7—cm distances are available as Sup. Pub. No. SUP 26082 (10 pages) from BLLD.

TABLE 1

Experimental conditions			
Nozzle to plate, distance, cm	21.091	11.122	6.560
Diameter of Pt nozzle, mm	0.25	0.25	0.25
Nozzle to beam distance, mm	0.45	0.45	0.45
Sample reservoir temperature, °C	-106.0	-106.0	-106.0
Estimated sample pressure, torr	25.0	25.0	25.0
Sector used (radius, mm)	r ³ (48)	r ³ (48)	r ³ (48)
Exposure time, seconds	4.0	7.0	20.0
Number of plates used	5.0	5.0	5.0
Accelerating voltage, kV	40.0	40.0	40.0

0.00262 Å for S—F and 0.00063 Å for F···F (*cis*) calculated by Brunvoll [8] were adopted in all refinements.

RESULTS

The experimental and final calculated molecular intensity curves are shown in Fig. 1, and the radial distribution function in Fig. 2. Derived

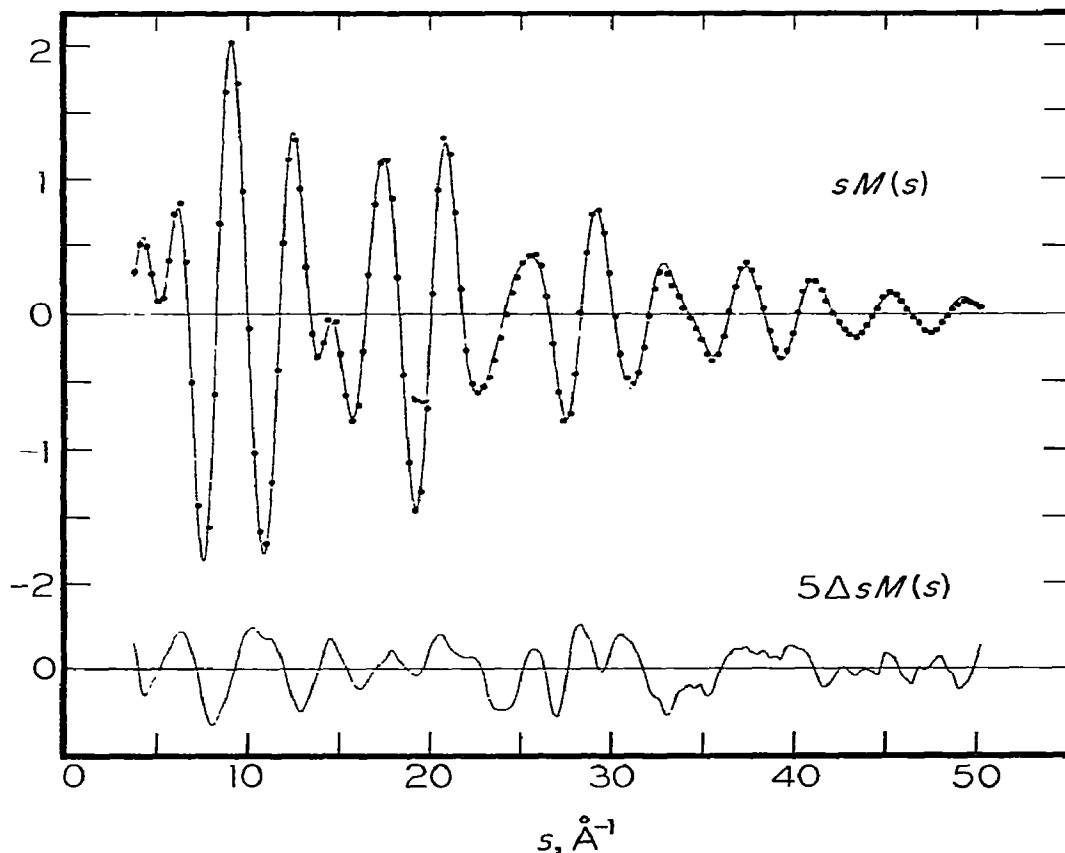


Fig. 1. Experimental (dots) and calculated (smooth curve) molecular intensity functions for SF₆; $\Delta sM(s) = sM(s)_{\text{expt}} - sM(s)_{\text{calc}}$.

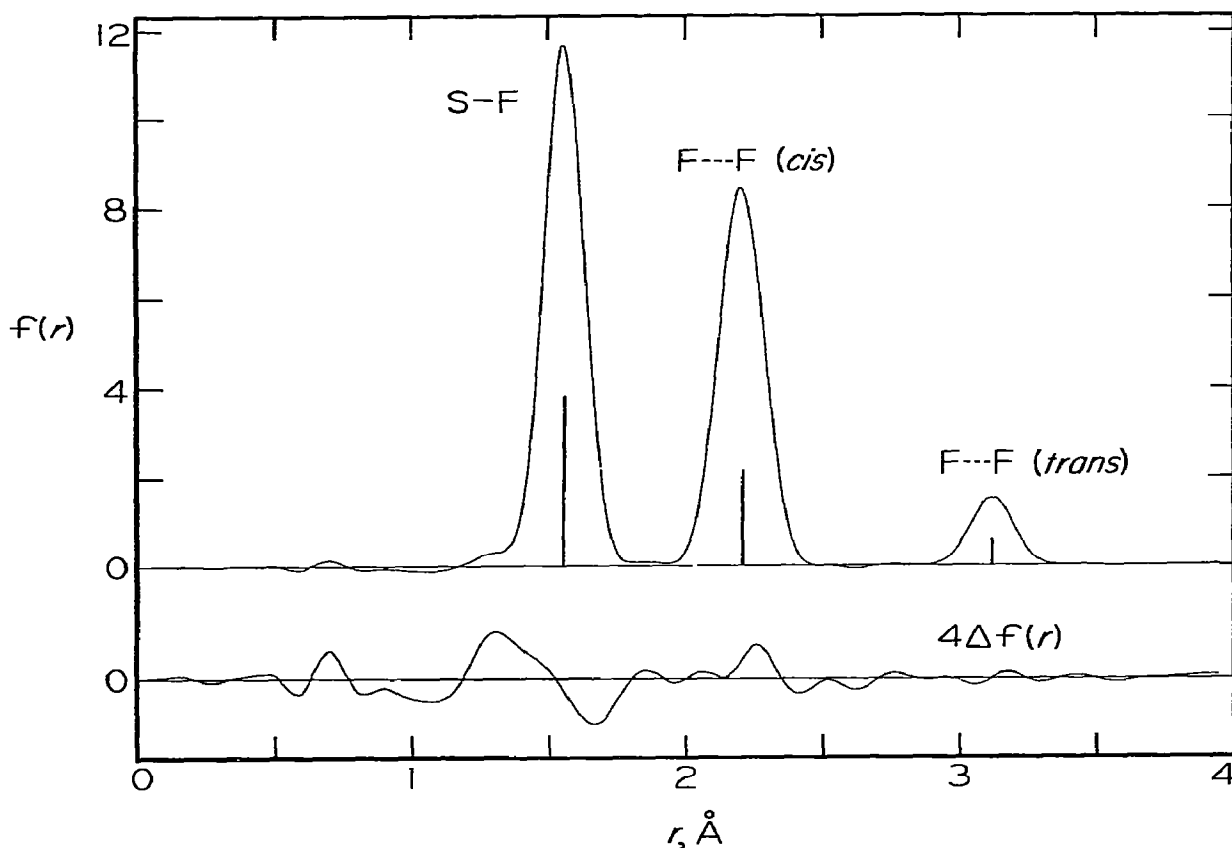


Fig. 2. Experimental radial distribution function for SF_6 ; $\Delta f(r) = f(v)_{\text{expt}} - f(r)_{\text{calc}}$.

molecular parameters are presented in Table 2. The correlation matrix is given in Table 3.

DISCUSSION

Observed and calculated [8] amplitudes of vibration are in satisfactory agreement. The bond length of 1.561 Å is appreciably shorter than the 1.568 ± 0.001 Å mean S—F bond length in SF_5Cl consistent with expectations of the VSEPR theory [7]. In the most primitive VSEPR interpretation, it might appear that the axial S—F bond length in SF_5Cl should closely resemble that in SF_6 . Equatorial S—F bonds in SF_5Cl , however, would be expected to be lengthened, relative to those in SF_6 , by the effect of the adjacent, less electronegative ligand Cl. This lengthening is, indeed, observed. It turns out, contrary to the zeroth-order guess, that the axial S—F bond in SF_5Cl is even longer. This additional lengthening has been interpreted as a “secondary relaxation effect” arising as a consequence of the “repulsion” of the equatorial fluorines by the chlorine [1, 9]. As the ClSF_{eq} angle relaxes to its equilibrium angle in excess of 90° , an increasing

TABLE 2

Derived molecular parameters and estimated errors^a for SF₆

Parameters	r_g (Å)	l_g (Å)
S—F	1.561 ± 0.002	0.044 ± 0.001
F...F <i>cis</i>		0.061 ± 0.002
F...F <i>trans</i>		0.056 ± 0.006

Index of resolution, nozzle to plate distance, sector 0.89 (21 cm, r^3), 0.83 (11 cm, r^3), 0.85 (7 cm, r^3)

^aEstimated uncertainties represent 3σ and include random and suspected systematic errors and our estimate of the effects of correlation between neighboring data points (with $\gamma = 1.2$ Å). Systematic standard errors are estimated to be 2 parts per ten thousand in wavelength measurement, 3 parts per ten thousand in nozzle to plate distance measurement, 2 parts per ten thousand in radial measurement in microphotometer scanning.

TABLE 3

Matrix of correlation coefficients for SF₆^a

	r_{SF}	l_{SF}	$l_{FF\ cis}$	$l_{FF\ trans}$	R^b
σ	0.00032	0.00047	0.0021	0.00063	0.0079
r_{SF}	100	5	4	1	6
l_{SF}		100	3	6	58
$l_{FF\ cis}$			100	5	49
$l_{FF\ trans}$				100	10
R					100

^aUnits for σ are Å for distances and amplitudes. Matrix elements are given by $\rho_{ij} = (M_x^w)_{ij} / [(M_x^w)_{ii} (M_x^w)_{jj}]^{1/2}$, where M_x^w corresponds to the error matrix of Bartell and Anashkin [J. Mol. Struct., 17 (1973) 193] for Markovian noise. All entries, except σ have been multiplied by 100. ^bIndex of resolution.

stress is brought to bear on the axial fluorine. The present information is pleasingly consistent with this interpretation. Since the nonbonded distances in SF₅Cl and SF₆ are closely comparable to the sums of the nonbonded radii of tightly packed atoms as suggested by Bartell [10] and Glidewell et al. [11], a significant proportion of the intramolecular stress may be atom—atom in origin rather than bond—bond as hypothesized in the VSEPR theory.

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