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Chemical Valence in SF_4 and SF_4O

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A qualitative molecular orbital treatment is used to correlate the electronic structure with the observed molecular structures of SF_4 and SF_4O.

Das M. O.-Verfahren wurde auf SF_4 und SF_4O bei Vorgabe der geometrischen Struktur qualitativ angewendet und auf diese Weise Einblick in die Elektronenstruktur gewonnen.

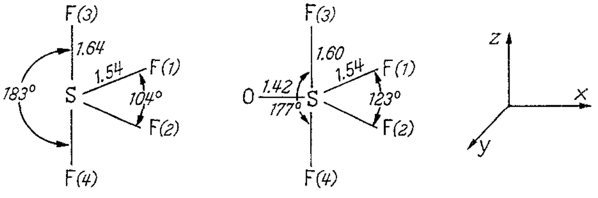
Un traitement qualitatif aux orbitales moléculaires met en corrélation la structure électronique et la géometrie observée de SF_4 et SF_4O.

Introduction

Recently Kimura and Bauer have determined the molecular structures of SF_4 and SF_4O by electron diffraction [*4*]. These compounds contain apparently overfilled shells and thus belong to the class of compounds which appear to violate the octet rule. With the discovery of the various rare gas compounds, it has been one of the prime requisites of valence theory that it be able to explain the stereochemistry of all compounds which contain apparent overfilled shells. Two approaches have been proposed in discussing the valency in these compounds. Gillespie and Nyholm [*3*] have advocated the use of outer *d* orbitals in the formation of bonds and stressed the roles of electron repulsions, especially of lone pairs, in determining the stereochemistry of chemical compounds. Rundle [*5*,*6*], on the other hand, has recently shown that a qualitative molecular orbital treatment can account for the principal features of these compounds without the use of outer *d* orbitals. It seems likely that the actual situation lies somewhere between these two extremes. In particular, an approach that combines the molecular orbital concepts of the Rundle scheme and the electron repulsion concepts of the Gillespie and Nyholm approach should yield a powerful valence theory for discussing molecular structure. This is the method which will be used to discuss the structures of SF_4 and SF_4O.

Molecular Orbital Treatment

Both molecules have C_{2v} symmetry with the two-fold axis in the x-direction and mirrors perpendicular to the y and z axes. See Fig. 1 for definition of the



a) SF_4 b) SF_4O

Fig. 1. Illustration of SF_4 and SF_4O molecules

coordinate systems. The irreducible representations for the C_{2v} group are a_1, a_2, b_1, and b_2. The orbitals belonging to each irreducible representation are given in the table. For the ligands, only σ orbitals are included since although π-bonding undoubtedly will be present, it should be of secondary importance.

Table. SF_4 *and* SF_4O *orbitals for the group* C_{2v}

Representation	Central atom orbitals	ligand sigma orbitals
a_1	$3s$, $3p_x$	$\sigma_1 + \sigma_2$, $\sigma_3 + \sigma_4$, σ_5[a]
a_2	*None*	*None*
b_1	$3p_y$	$\sigma_1 - \sigma_2$
b_2	$3p_z$	$\sigma_3 - \sigma_4$

[a] This orbital is present only for the SF_4O molecule.

It is seen that the $3p_x$ orbital is essentially orthogonal to the $\sigma_3 + \sigma_4$ orbital since F (3) and F (4) lie almost directly along the z-axis. Also the $3s$ orbital will interact less strongly with the $\sigma_3 + \sigma_4$ orbital than with the $\sigma_1 + \sigma_2$ and the σ_5 orbitals because of the longer bond distances along the axial direction. The molecular orbital energy level scheme obtained is given in Fig. 2. The a_1 and b_1 molecular orbitals involve bonds between the sulfur and the equatorial fluorine atoms while the b_2 molecular orbital is a delocalized bonding orbital spread along the z-axis. The a_1' molecular orbital is essentially a non-bonding orbital comprised mainly of the $\sigma_3 + \sigma_4$ orbital with some contribution from the $3s$ orbital. The a_1'' orbital (present only in SF_4O) corresponds to the S-O bond while the $a_1^{*\prime}$ orbital in SF_4 corresponds to a lone pair as it is essentially a sp^2 hybrid.

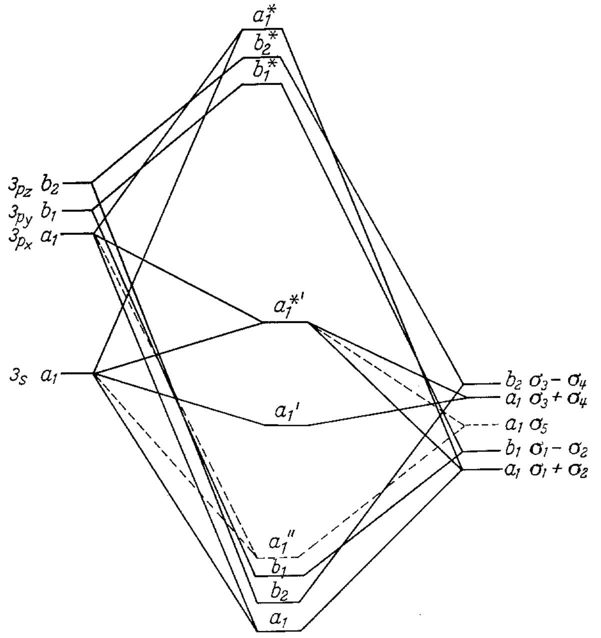


Fig. 2. Molecular orbital energy scheme for SF_4 and SF_4O. Energy levels not drawn to scale. The molecular orbitals involving oxygen atomic orbitals are shown by dashed lines

Qualitative Valence Description

In SF_4, the electronic configuration is $(a_1)^2(b_2)^2(b_1)^2(a_1')^2(a_1^{*\prime})^2$. Thus, in valence bond terms, essentially sp^2 hybridization is involved in the equatorial plane. The two electrons in the lone pair orbital ($a_1^{*\prime}$), because of their repulsive effects, compress the F (1)-S-F (2) bond angle to 104°. In the axial direction, one bonding MO and one non-bonding MO are formed. There are two axial S-F bonds but only one bonding orbital is occupied, thus explaining the increased bond lengths in the axial direction (1.64 Å) over the bond lengths in the equatorial direction (1.54 Å). This is also supported by the weaker force constants for the axial bonds ($2.077 \times 10_5$

dyne/cm) than for the equatorial bonds (5.346 × 10- dyne/cm)^2. This combination of bonds along the axial direction is equivalent to two one-electron bonds. The influence of the lone pair is less marked on the F (3)-S-F (4) bond angle, the observed angle being 183° and the longer axial bond distances presumably account for this smaller steric affect. It is expected that the axial bonds will be stabilized when the ligands are highly electronegative and have a tendency to draw electrons away from the central atom. This is illustrated in $TeCl_2(CH_3)_2$ [*4*], where the chlorine atoms are in the axial positions and the methyl groups are equatorial.

The electronic configuration in SF_4O is $(a_1)^2(b_2)^2(b_1)^2(a_1'')^2(a_1')^2$. Again, the sulfur atom can be described as being in essentially a sp^2 state. Since the electrons corresponding to the lone pair electrons in SF_4 are now involved in the formation of the S-O bond, the main aspects of steric repulsion are absent and the F (1)-S-F (2) bond angle is 123°, almost exactly the predicted 120°. The F (3)-S-F (4) bond angle is 177° and is nearly linear again as expected. The axial S-F bond (1.60 Å) is slightly shorter than in SF_4.

Conclusion

The principal features of the valence in "electron rich" compounds, as illustrated by SF_4 and SF_4O, can be understood satisfactorily in terms of a qualitative molecular orbital approach without the involvement of outer *d* orbitals.

From a group theoretical analysis, it is evident that the *d* orbitals have the proper symmetry to be used in the formation of bonds and since it is necessary to use *d* orbitals in order to obtain an accurate description of methane, it is equally obvious that they will make some contribution to the wave functions in SF_4 and SF_4O. In particular, it may be argued that the "non-bonding" axial orbital will be stabilized by a contribution from the $3d_{z^2}$ orbital of the sulfur and it undoubtedly is to some extent; however, the contribution *cannot* be large since this involves the transfer of electrons from electronegative fluorine atoms to a sulfur *d* orbital. If the *d* orbital contribution was important, it would be expected that the oxygen should occupy an axial position because of its lower electronegativity. A discussion of π-bonding, and the involvement of *d* orbitals therein, has not been given, although this may have an effect on such physical properties as the charge distribution.

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