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The Electronic Structure of Chlorine Trifluoride: An Approximate MO-LCAO-SCF Calculation*

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Calculations have been performed on ClF_3 using an approximation scheme previously developed by the author. Only valence shell *s* and *p* orbitals are used in the basis. It is found that the *T*-shaped nuclear configuration can be satisfactory explained without the use of chlorine 3*d* orbitals. The calculated charge distribution is found to be similar to that postulated by the Gillespie and Nyholm model but with excess electronic charge on the fluorine atoms.

Rechnungen am ClF_3 werden nach einem angenäherten SCF-Verfahren durchgeführt, wobei als Basis nur *s*- und *p*-Funktionen verwendet werden. Dabei zeigt sich, daß sich die *T*-Konfiguration des Moleküls auch ohne Einbeziehung von 3*d*-Zuständen des Chlors ergibt. Die erhaltene Ladungsverteilung entspricht der des Modells von Gillespie und Nyholm, jedoch mit größerer Elektronendichte am Fluor.

ClF_3 a fait l'objet de calculs selon un schéma développé précédemment par l'auteur. La base ne contient que les orbitales *s* et *p* des couches de valence. La configuration nucléaire en forme de *T* peut être expliquée d'une manière satisfaisante sans l'utilisation des orbitales 3*d* du chlore. La distribution de charge calculée est similaire à celle postulée dans le modèle de Gillespie et Nyholm avec cependant un excès de charge sur les atomes de fluor.

1. Introduction

Bond angles of electron-rich molecules are predicted qualitatively by means of the Gillespie and Nyholm model of bond-pair — lone-pair repulsions [*6*]. This model is largely intuitive and mainly related to valence-bond theory using hybridized atomic orbitals. In order to form electron pairs in the desired direction it is often thought to be necessary to use orbitals unoccupied in the ground state of the atom. Thus for phosphorus, sulfur, chlorine, and heavier non-metals it is assumed that unoccupied *d*-orbitals are important for binding.

There are very few quantum mechanical calculations on electron-rich molecules, mainly because their size makes them intractable with accurate techniques. Havinga and Wiebenga calculated ClF_3 and other interhalogen compounds in a Hückel-type approximation with only $p\sigma$-bonding [*7*]. Their results give the correct order of bond-lengths from bond-order considerations, but no attempt was made to vary the bond angles. Ali [*2*] used Murrell's method [*16*] to construct best hybrid orbitals but found using the maximal overlap criterion for binding that the planar regular configuration would be more stable than the *T*-shape

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experimentally determined [*3*, *22*]. He also performed an approximate MO–LCAO–SCF calculation on the regular form and found it not to have a Jahn-Teller distortion. Volkov and Dyatkina [*24*], also using a method of maximum overlap but not including $3d$ orbitals on chlorine, got however a stable configuration in agreement with experiment.

In order to treat the bond angle problem further we report in this paper a series of calculations on ClF_3 in various nuclear configurations but with fixed chlorine-fluorine bond lengths. The method used is an approximate MO–LCAO–SCF method previously developed by the author [*11*]. For a full description of the approach we refer to this paper and give here only those details pertinent to this specific calculation.

2. Method

Only valence shell s and p orbitals were used in the basis formed from Clementi's ground state atomic SCF orbitals [*4*] orthogonalized against core orbitals on the other atoms. The coordinate systems for p orbitals were chosen with parallel axes (see Fig. 1). In this way it can be made relatively simple to change the molecular geometry, but on the other hand the basis set is in general not symmetry adapted. Overlap and kinetic energy integrals were calculated rigorously and the atomic orbital energies used were those calculated by Clementi [*4*]. Many-center integrals were treated in the simplest possible manner. Only penetration integrals of the types $(U_g \mid s_h s_h)$, $(U_g \mid \sigma_h \sigma_h)$, and $(U_g \mid \pi_h \pi_h)$ were included and calculated rigorously. Here σ_h is a valence shell p orbital on atom h pointing towards atom g and π_h is similarly a p orbital on h perpendicular to the g-h direction. Since these integrals are very different from each other the Ruedenberg approximation was used for the Coulomb part of them. The exchange part of penetration integrals were treated in the same way as the remaining electron interaction terms, i.e. with the Mulliken approximation which reduces all integrals involved to those of simple Coulomb type. These were further approximated by a formula first proposed for π-electrons by Ohno [*17*]

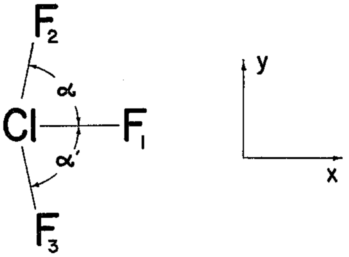

Fig. 1. Molecular geometry of ClF_3. The z-axis is chosen perpendicular to the molecular plane. In the calculations reported here α' has been chosen equal to α

Table 1. *Parameters for one-center Coulomb repulsion integrals (in Hartrees)*

Cl	$[3s \mid 3s]$	0.4563
	$[3s \mid 3p]$	0.4118
	$[3p \mid 3p]$	0.4232
F	$[2s \mid 2s]$	0.5098
	$[2s \mid 2p]$	0.5517
	$[2p \mid 2p]$	0.5706

$$\gamma_{ij} = 1/(a^2 + R_{ij}^2)^{1/2}$$

where $1/a = (\gamma_{ii} + \gamma_{jj})/2$ and R_{ij} is the internuclear distance. Hartree atomic units are used throughout. The remaining one-center integrals γ_{ii}, were estimated from valence state ionization potentials calculated by Hinze and Jaffe [*8*] from experimental data using the "$I - A$" approximation of Moffitt and Pariser

[*13, 18*], well known in π-electron theory. Finally, integrals involving p orbitals in various directions were averaged in order to preserve the molecular symmetry under the Mulliken approximation. Of the core-valence interaction elements only orthogonalization terms were kept, and all core-core interactions were neglected. Some of these approximations can be justified theoretically, others not. In particular, the treatment of electron interactions is deliberately superficial, but with the main part of the effective Hamiltonian accounted for in a fairly rigorous way it was felt that over-all ground state properties could still be predicted with some accuracy.

The point group of ClF_3 is C_{2v} with the symmetry axis in the Cl–F_1 bond and with atoms F_2 and F_3 equivalent to each other (see Fig. 1). The irreducible representations were labelled so that a_1 and b_1 are symmetric (σ) and a_2 and b_2 antisymmetric (π) with respect to reflexions in the molecular plane.

Calculations were performed for 12 planar configurations with the bond angle α varying from 60 to 120 degrees. All chlorine-fluorine distances were kept equal to 3.123 a.u. (1.653 Å) being the mean value of the bond lengths determined by BURBANK and BENSEY [*3*] in the solid state. For $\alpha = 120°$ the point group of the molecule is D_{3h} with the three-fold axis along the chlorine z-axis. In this case representations a'_1, a'_2, and e' have σ symmetry and a''_2 and e'' π symmetry.

3. Results

It is well known that the Hartree-Fock approximation gives a negative binding energy for the fluorine molecule but still gives a quite good equilibrium bond length and other molecular properties [*20, 25*]. In the light of this fact and since our main interest was in calculating the bond angle, we have not calculated the total binding energy of the molecule, but only the energy relative to the symmetric configuration ($\alpha = 120°$). This is greatly simplified with the use of constant chlorine-fluorine bond lengths.

The equilibrium angle is estimated from Tab. 2 to be $\alpha = 79.2°$ with an energy 0.35050 Hartrees below that of the symmetric configuration. This bond angle is in satisfactory agreement with the experimental value of $\alpha = 87.0°$ [*5*]. The bending

Table 2. *Distortion energies and Mulliken valence electron gross atomic populations*

α	ΔE	p(Cl)	$p(F_1)$	$p(F_{2,3})$
60	0.01180	5.7464	7.4441	7.4047
65	−0.17404	5.7277	7.4291	7.4216
70	−0.28977	5.7217	7.3981	7.4400
75	−0.33939	5.7221	7.3629	7.4575
78	−0.34975	5.7230	7.3418	7.4647
80	−0.35022	5.7236	7.3275	7.4744
82	−0.34683	5.7240	7.3137	7.4812
87	−0.32024	5.7218	7.2800	7.4991
95	−0.23948	5.7027	7.2321	7.5326
105	−0.10241	5.6212	7.2152	7.5818
115	−0.00923	5.5340	7.3783	7.5439
120	—	5.5278	7.4906	7.4908

Table 3. *σ-electron population analysis for α = 87°*

		Cl			F_1			$F_{2,3}$		
		$3s$	$3p_x$	$3p_y$	$2s$	$2p_x$	$2p_y$	$2s$	$2p_x$	$2p_y$
Cl	$3s$	1.8405								
	$3p_x$	0.0005	1.1003							
	$3p_y$	0.	0.	0.4718						
F_1	$2s$	0.0193	−0.0239	0.	1.9174					
	$2p_x$	0.1216	0.2575	0.	0.0005	1.2573				
	$2p_y$	0.	0.	−0.0009	0.	0.	2.0107			
$F_{2,3}$	$2s$	−0.0724	0.0049	0.0446	−0.0025	−0.0098	−0.0060	1.9246		
	$2p_x$	−0.0033	−0.0257	0.0013	−0.0050	−0.0068	−0.0076	0.	2.0129	
	$2p_y$	−0.0717	0.0161	0.2282	−0.0146	−0.0331	−0.0073	0.0003	0.	1.5404
gross		1.7638	1.2126	0.7454	1.8932	1.3974	1.9894	1.9055	1.9893	1.6043

force constant is however calculated to 2.5 mdyn/Å, compared with the experimental value of 0.69 mdyn/Å determined by LONG and JONES [*10*] from the vibrational spectrum. Though the latter value has a considerable experimental uncertainty it seems less likely that this fact alone can make up for the difference. One might therefore assume that the calculated energy minimum is somewhat deeper than in reality. The distortion energy and the molecular orbital energies with their symmetry assignments are plotted in Fig. 2.

A Mulliken population analysis [*15*] has been performed for the experimental equilibrium configuration (α = 87°). The main part of Tab. 3 contains net orbital

Table 4. *Overlap populations between* F_2 *and* F_3

	$2s$	$2p_x$	$2p_y$
$2s$	0.0002	0.	0.0024
$2p_x$	0.	0.	0.
$2p_y$	0.0024	0.	0.

and overlap populations with the gross orbital population at the bottom of each column. The p_z orbitals have been omitted since they are fully occupied. The small overlap populations that appear in some cases between orbitals on the same atom are due to a non-orthogonality resulting from the projection against inner orbitals on adjoining atoms. Overlap populations between F_2 and F_3 are reported in Tab. 4. Tab. 1 further contains valence electron gross atomic populations for all calculated bond angles. No significant change of these quantities with bond angle is shown.

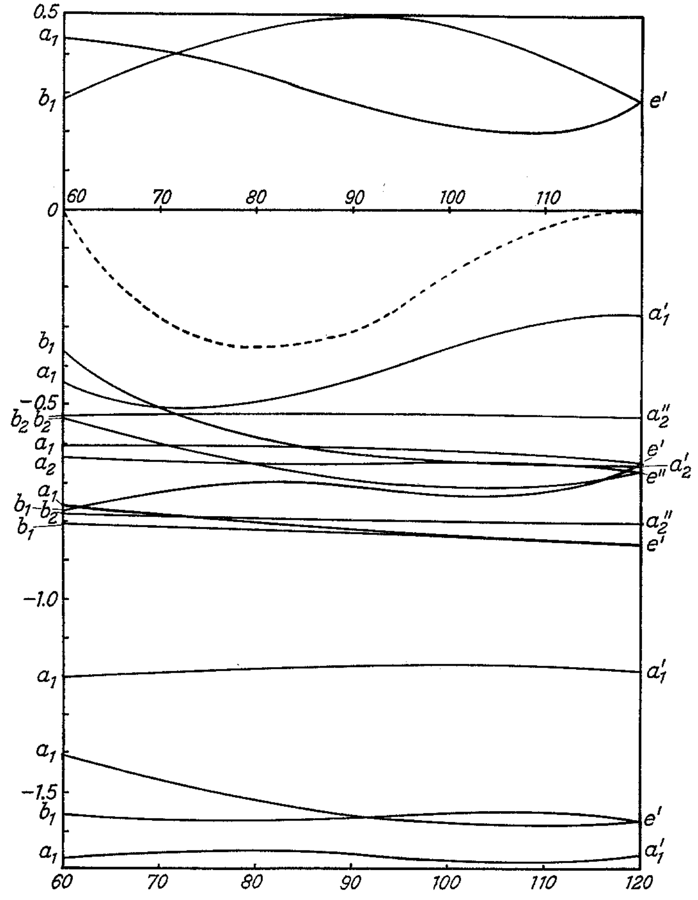

Fig. 2. Orbital energies and distortion energy (dotted) as functions of the bond angle α. Energies in Hartree atomic units

4. Discussion

A classification of the molecular orbitals for the regular planar configuration of an AB_3 molecule has been given by WALSH [*26*]. With the basis system employed here there are 16 molecular orbitals to consider, 12 of which are symmetric (σ) and 4 antisymmetric (π) with respect to reflection in the molecular plane. Starting from the lowest energy we can classify the σ orbitals into 3 fluorine $2s$ orbitals, 3 chlorine-fluorine bonding orbitals, 3 fluorine non-bonding orbitals perpendicular to the bond directions, and 3 antibonding orbitals. The π orbitals are likewise classified into 1 bonding orbital, 2 fluorine non-bonding orbitals and 1 antibonding orbital. In a 28 electron system like ClF_3 only the two highest antibonding σ-orbitals are unfilled. For a planar distorted molecule it can be seen from Fig. 2 that the most marked difference is the lowering of the energy of the highest occupied molecular orbital, while that of the other occupied orbitals stays more or less constant. With smaller bond angles the lone pair interactions however spread their energies with a net increase in electronic energy as effect.

A simple description of the shape of the higher orbitals of the molecule in its equilibrium configuration is not possible. However, the population analysis throws considerable light on the charge distribution. First to be noted is the polar character of the chlorine-fluorine bonds, with excess electronic charge on the more electronegative fluorine atoms. As is also clear from the molecular orbital structure all π orbitals are doubly occupied and do not contribute to the bonding. There is a large off-diagonal term in the first order density matrix (not shown here) between chlorine $3s$ and $3p_x$ orbitals which thus can be transformed into natural hybrids in MCWEENY's sense [*12*] of *sp* type. The one with the higher population is directed away from F_1, and can be described as a lone pair, the other forms a Cl–F_1 bond pair with a similar hybrid on F_1. Bond pairs can be formed between chlorine and the two remaining ligands if one splits the Cl $2p_y$ orbital into its two lobes. Thus it is possible to give a description of the charge distribution similar to the Gillespie and Nyholm model without using Cl $3d$ orbitals.

The role of sulfur $3d$ orbitals in N_4S_4 was recently discussed by TURNER and MORTIMER [*23*]. They found from calculations in the Wolfsberg-Helmholz approximation that no major changes occur in ground state properties if $3d$ orbitals are excluded. Though no calculations with chlorine $3d$ orbitals have been made here it still seems clear that they are not essential for the determination of chlorine trifluoride bond angles. However, a basis set involving $3d$ as well as other unoccupied atomic orbitals is of course necessary if accurate solutions to the SCF equations are desired. Particularly, if the electronic spectrum is to be calculated, the present basis set, which gives only two unoccupied orbitals, seems to be too limited.

The NMR spectrum of fluorine in ClF_3 has been called anomalous since the chemical shifts indicate a greater covalent character of the Cl–$F_{2,3}$ bonds than of the Cl–F_1 bond [*14, 1*]. A similar anomaly exists for the ClF molecule where simple theory gives a negative fluorine charge larger than -1. This latter anomaly appears to be resolved if the customary assumption of an average excitation energy is not used in the second-order perturbation term considered most important for the chemical shift [*21, 5*]. Exploratory calculations with the simple theory of KARPLUS and

Das [9] thus amended do however not give the desired ordering. Since the covalent character as calculated here is in accord with the experimental bond lengths it seems likely that the answer to the problem is to be found in the theory of chemical shifts rather than in the molecular charge distribution. In particular, a theory of chemical shifts that accurately accounts for effects from neighboring atoms would be desirable.

Bond angles of smaller polyatomic molecules have been calculated by Pople and Segal [19] using similar methods as here but with neglect of differential overlap. In the light of their results the success of the present calculation is not astonishing. However, their methods employ semiempirical bond parameters which are adjusted to experimentally known properties of other, usually diatomic, molecules. In that way large classes of more or less similar molecules can be calculated sometimes with rather high accuracy. For a unique molecule, like the one treated here, it may be difficult to obtain parameters without reducing the whole calculation to curve-fitting. In such a case our method appears to be particularly useful. The only empirical estimate, that of Coulomb repulsion integrals, is included only as a matter of convenience. It is known to give integrals smaller than those calculated theoretically, and thus gives better agreement with the experimental π-electron spectrum of conjugated molecules. In the present case the repulsion between the negatively charged fluorine atoms is reduced. One may therefore speculate that this is one of the reasons why the calculated bond angle is smaller than the experimental value. The least one can say therefore is that a calculation using exact repulsion integrals will probably not give fundamentally worse bond angles than obtained here.

It is intended to extend calculations of the type used here to other electron-rich molecules, notably xenon fluorides.

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