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Electronic structure of small fluorocarbon clusters $F_pC_n$ ($p = 1, 2$) observed in secondary ionic mass spectrometry (SIMS). II. Electronic populations and F-C bonding

M. Leleyter (*)

Groupe de Physique Théorique, Faculté des Sciences, 33, rue Saint-Leu, 80039 Amiens Cedex, France

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Résumé. — On utilise un calcul CNDO pour interpréter à partir d’un modèle de chaîne linéaire les alternances dans les intensités d’émission secondaire des ions $F_pC_n^\pm$ ($p = 1, 2$), avec renforcement des ions $F_pC_{2k}^{+1}$ et $F_pC_{2k}^{-1}$. Le calcul montre que le très fort effet « pair-impair » provient du fait que le « niveau de Fermi » (« HOMO ») des agrégats supposés être des chaînes linéaires $C_n$ avec un ou deux atomes de fluor liés à l’une ou aux 2 extrémités des chaînes, tombe dans une bande de niveaux $\pi$ dégénérés. L’étude des oscillations de charge le long de la chaîne montre qu’elles sont directement liées à la parité du nombre d’atomes de carbone et par suite au remplissage du niveau de Fermi : il y a des oscillations pseudo-périodiques uniquement pour les agrégats les plus stables ; dans les autres cas, les charges ne montrent plus de comportement périodique. La distribution des charges donne aussi d’intéressantes informations sur la liaison F-C et met en évidence le fait que la forte électronégativité du fluor joue un rôle essentiel.

Abstract. — A CNDO calculation is used to interpret from a linear chain model the alternations in the emission intensities of secondary $F_pC_n^\pm$ ions ($p = 1, 2$) with enhancements of $F_pC_{2k}^{+1}$ and $F_pC_{2k}^{-1}$ ions. The calculation shows that the strong even-odd effect arises from the fact that the Fermi level (« HOMO ») of the clusters, assumed to be linear $C_n$ chains with one or two F atoms related to one or both ends of the chains, falls into a band of degenerate $\pi$ levels. The study of the charge oscillations throughout the chains shows that they are directly related to the carbon atom number parity and therefore to the filling of the Fermi level : there are damped periodic oscillations only for the most stable clusters ; in the other cases the charges do not show any periodic behaviour. The distribution of the charges gives interesting information on the F-C bond too and points out that the strong F electronegativity plays an essential role.

1. Introduction.

In the previous paper [1] (hereafter referred to as I), the stabilities of $FC_n$ and $F_2C_n$ chains were computed with the CNDO procedure and compared to experimental results on SIMS of teflon (P.T.F.E.). We found a fairly good agreement between the stability variations of linear $F_pC_n$ chains against $n$ and the oscillations in emission intensities of $F_pC_n^\pm$ ions, that is, a very pronounced even-odd effect in both cases with very large maxima for odd $n$ (positive ions) or even $n$ (negative ions).

We shall now study how the oscillations of the relative stabilities of the clusters pointed out in I are bound to the electronic charge oscillations throughout the carbon chain and on the impurity atom (or atoms).

The analysis can be carried out from two points of view : we can either study the variation of the charge on the fluorine atom or on the adjacent F and C atoms for all $n$, or consider the variation of the electronic population for an $F_pC_n$ chain of given $n$ on every atom of the chain versus its position along the chain and its nature, F or C. Figures 1 and 2 illustrate the first point of view and figures 3 and 4 the second one. In the latter case, we have also recalled the charge variations through the $C_n$ chains to make comparison easier.
2. Study of F atom (or F atoms) against n. F-C bonding.

2.1 FCₙ CHAINS. — In figure 1, we represent versus n the difference Q between the charges of the fluorine atom and the 2 adjacent carbon atoms C₁ and C₂, and the charges of the corresponding free neutral atoms (only for the cumulene type chain defined in (I) to keep the same structure whatever n). We see that the fluorine atom has a small negative charge which keeps almost the same value for all the FCₙ chains; thus it is always electron-attracting. On the contrary, the lack of electron on the atom C₁ adjacent to the fluorine shows interesting alternations, with a larger deficit for odd n which particularly comes from the π electrons, as can be seen when analysing the electronic population. This fact is only reflecting the variations of the Fermi level filling, which we mentioned in I (Sect. 3.3.1.1). In connection with this filling, we observe that for atom C₂, Q is alternating around the zero value and this is also due to π electrons. These two results agree with the position of HOMO in the π band fairly well.

For C₁ in FC₆, we have in the same way:

\[ 2s\sigma = 1.8378, \quad 2p\sigma = 1.3635, \quad 2p\pi = 3.9068. \]

In comparison with the free F atom, these results show that fluorine is a strong π electron-acceptor and a strong σ electron-donor.

To sum up, this discussion well corroborates the energy level analysis in I (Sect. 3.3.1.1).

Table I. — CNDO electron charge densities ρ on the atoms in the FC₅ and FC₆ chains and their decomposition according to local symmetry (σ or π).

<table>
<thead>
<tr>
<th>FC₅</th>
<th>F</th>
<th>C₁</th>
<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>C₅</th>
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<tr>
<td>s</td>
<td>1.8377 1.0732 1.0169 1.0735 1.0427 1.6493</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>5.2668 2.7176 3.0451 2.7523 3.0690 2.4561</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>σ</td>
<td>3.2022 1.8745 2.0350 2.0741 1.9972 2.9070</td>
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</tr>
<tr>
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<table>
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<th>FC₆</th>
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<th>C₂</th>
<th>C₃</th>
<th>C₄</th>
<th>C₅</th>
<th>C₆</th>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p</td>
<td>5.2703 2.7834 2.9543 2.9883 2.7850 3.0396 2.4553</td>
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<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>σ</td>
<td>3.2013 1.8612 1.9611 1.9814 2.0777 2.0097 2.9077</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>π</td>
<td>3.9068 1.9863 2.0169 2.0353 1.7809 2.0772 1.1967</td>
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<td></td>
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</tr>
<tr>
<td>ρ</td>
<td>7.1081 3.8474 3.9779 4.0167 3.8585 4.0870 4.1044</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2 F₂Cₙ AND FCₙF CHAINS. — In figure 2 the fundamental difference in the charge behaviour of the 3 series of isomers immediately appears.

The electronic configuration of F in FC₆ (cumulene) is \( s^{1.84}p^{5.27} \) and that of C₁ is \( s^{1.06}p^{2.78} \) (Tab. I) (the values for the triacetylenic molecule are almost the same), a sign of a significant sp hybridization. We can then conclude that our model of linear chains with sp hybridization gives a fairly good interpretation of experimental data on FCₙ.

The electronic populations of the fluorine atom orbitals in FC₆ are the following (Tab. I):

\[ 2s\sigma = 1.8378, \quad 2p\sigma = 1.3635, \quad 2p\pi = 3.9068. \]

For C₁ in FC₆, we have in the same way:

\[ 2s\sigma = 1.0641, \quad 2p\sigma = 0.7971 \text{ and } 2p\pi = 1.9863. \]

To sum up, this discussion well corroborates the energy level analysis in I (Sect. 3.3.1.1).
For the symmetrical isomers (middle part of Fig. 2), the « charges » (excess on F, lack on C) are practically independent of \( n \). On the contrary, in the disymmetrical linear isomer case (left part of Fig. 2), the charges of the terminal F atom and of C₁, the carbon atom adjacent to the 2 F, have large oscillations when \( n \) varies, but of opposite signs. Atom F₂ has charge variations of the same kind as F₁, but much weakened. In the non linear case (right part of Fig. 2), one observes an intermediate behaviour: F atoms always remain electron-attracting and C atom electron-donating whatever \( n \). However, the C charge shows alternations almost exactly as in the disymmetrical linear case.

From figure 2 for linear \( F₂Cₙ \), it is obvious that if \( n \) is odd (which is the case of larger cluster stability), the terminal atom F₁ is very strongly electron-attracting and that if, on the contrary, \( n \) is even, it is strongly enough electron-donating. This fact is even more obvious in table II where the whole charge \( \rho \) on the different atoms of \( F₂C₅ \) and \( F₂C₆ \) is given. Table II also shows that on F₁, there is little sp hybrid character for the disymmetrical linear isomers (we have indeed for \( F₁ s^{1.97}p^{5.08} \) in \( F₂C₅ \)), but the sp character is larger for the symmetrical clusters (in \( F₇C₆F \) we have this time on \( F₁ s^{1.84}p^{5.28} \)) and for the non linear clusters (non given in Tab. II) with the configuration \( s^{1.84}p^{5.33} \) on F in \( F₂C₆ \).

Charges on atoms F₁ and C₁ thus seem to play a preponderant role in linear \( F₂Cₙ \) (while for non linear \( F₂Cₙ \) the important role is played by the charge on atom C₁). This simply shows that the M.O. analysis done in I (Sect. 3.3.2) can be improved by considering that the orbitals which we called \( \sigma_L(F-F) \) or \( \sigma_L(F-C) \) or \( p\sigma_F \) are in fact spread out on the 3 atoms F₁, F₂ and C₁ (as in the non linear case). The analysis in I has the advantage of allowing us to understand how the atoms are bound to each other. However this is only a sketch which is complemented by the electronic population study.

Finally we can conclude from the population analysis that the atom charge alternations are, as could be expected, directly bound to the alternations of the relative stabilities of the fluorocarbon chains.

Table II. — CNDO electron charge densities \( \rho \) on the atoms in the \( F₂C₅, F₂C₆, FC₇F \) and \( FC₆F \) linear chains and their decomposition according to local symmetry (\( \sigma \) or \( \pi \)). For the symmetrical isomers, only half the table is given since the values of the charges are symmetrical.

<table>
<thead>
<tr>
<th>( F₂C₅ )</th>
<th>( F₁ )</th>
<th>( F₂ )</th>
<th>( C₁ )</th>
<th>( C₂ )</th>
<th>( C₃ )</th>
<th>( C₄ )</th>
<th>( C₅ )</th>
</tr>
</thead>
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<td>( s )</td>
<td>1.9682</td>
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<td>1.4601</td>
<td>1.0321</td>
<td>1.1204</td>
<td>1.0281</td>
<td>1.6510</td>
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<tr>
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<td>5.4159</td>
<td>4.9593</td>
<td>2.2951</td>
<td>1.9603</td>
<td>2.4689</td>
<td>3.1582</td>
<td>2.2926</td>
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<tr>
<td>( \sigma )</td>
<td>3.3865</td>
<td>3.0771</td>
<td>2.4994</td>
<td>3.6784</td>
<td>2.1809</td>
<td>1.9683</td>
<td>2.9274</td>
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<tr>
<td>( \pi )</td>
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<td>2.2180</td>
<td>1.0162</td>
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<td>( \rho )</td>
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<thead>
<tr>
<th>( F₂C₆ )</th>
<th>( F₁ )</th>
<th>( F₂ )</th>
<th>( C₁ )</th>
<th>( C₂ )</th>
<th>( C₃ )</th>
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<th>( C₅ )</th>
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<td>3.0088</td>
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<td>1.9945</td>
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<td>1.9870</td>
<td>2.9116</td>
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<tr>
<td>( \pi )</td>
<td>3.9960</td>
<td>3.9102</td>
<td>2.1326</td>
<td>1.8932</td>
<td>2.1638</td>
<td>1.6858</td>
<td>2.1651</td>
<td>1.1936</td>
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<td>3.8878</td>
<td>4.1156</td>
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<td>4.1052</td>
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<table>
<thead>
<tr>
<th>( FC₇F )</th>
<th>( F )</th>
<th>( C₁ )</th>
<th>( C₂ )</th>
<th>( C₃ )</th>
<th>( C₄ )</th>
<th>( C₅ )</th>
<th>( C₆ )</th>
<th>( C₇ )</th>
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<td>1.0279</td>
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<td>1.9846</td>
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<td>2.0532</td>
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<td>2.0189</td>
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<td>2.0054</td>
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<td>3.9845</td>
<td>3.9727</td>
<td>3.9609</td>
<td>3.9491</td>
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</tbody>
</table>

For that purpose, we first examine the one fluorine atom chains, then the 2-atom chains, with figures 3 and 4 and tables I and II.

3.1 FCₙ CHAINS. — In figure 3, we show the charge distribution on FCₙ chains and also as a comparison, the distribution on Cₙ chains with the same total atom number. As a matter of fact, we can consider FCₙ as a Cₙ₊₁ chain in which a terminal carbon atom is replaced by an « impurity », here a fluorine atom. Charge Q is, as before, the algebraic excess on a given atom with respect to its charge when it is free. For convenience sake in this study we have assumed that the charges are concentrated on every atom of the chain and not continuously distributed on the atoms and between them. We then have a drawing with angular points and not a smooth curve looking like a damped sine curve.

Fig. 3. — Oscillations of charge Q (in electron number) on the atoms in the Cₙ (n = 5-7) and FCₙ (n = 3-5) chains computed in CNDO.

It is known that such charge fluctuations on the linear chain atoms are a very general phenomenon and come from the existence of a « surface », that is the end of the Cₙ chain, and that this perturbation to the periodicity of the linear « crystal » gives rise to « Friedel oscillations » of period 2 k_F (k_F is the wave vector of the crystal at the Fermi level HOMO) rapidly enough shielded on the inside of the chain [2]. Friedel oscillations are the answer of the system to a localised perturbation (here the existence of a dangling bond at the end of the chain) which leads to an oscillation period bound to the charge density and not to the positions of the atoms along the chain [3]. It is then another way of taking account of the dangling bonds already described in I.

In the cases of C₅, C₆ and C₇ chains, the charge oscillations are of course perfectly symmetrical with respect to the middle of the chain and we observe a light electron excess at each end; the excess is however more pronounced for the even-n than for the odd-n chains, and it is directly connected to the filling of the « crystal » bands [4]. In the case of a sp band the Cₙ chains are exactly half-filled. If the band were less than half-filled, we would have a lack of electrons, thus a positive charge at the ends of the chains, this is the case when we examine a Cₙ chain [4, 5].

The charge behaviour through the Cₙ chains appears to be very different according to the parity of n. When n is odd, there are in particular very large oscillations on every atom. Everything seems to happen as if we had a distribution analogous to a system of « stationary waves » of the electronic charges which would be in phase with the « lattice » and therefore would be enhanced. On the contrary, when n is even, the oscillations are very much weaker because they seem to have a period incommensurable with the lattice period.

The analysis of FCₙ case shows that the oscillations are here the answer to a double perturbation: the existence of the surface and the presence of an impurity. As for Cₙ, there is an electron excess at each end of the chain (case of a sp band more than half-filled because of the 7 electrons of the fluorine). The sketch of course is no longer symmetrical, but we see a great analogy between the oscillations in C₅ (or C₇) and in FC₅, with congruence of their « pseudo-periods » to the atomic positions. On the contrary, FC₄ and FC₆, as C₆, do not lead to any periodicity of their charge oscillations which would be incommensurable with the crystal periodicity.

For Cₙ and FCₙ, we have commensurability and therefore an enhancement of the charge oscillations every time that n is odd (this is the case when the molecules are the most stable). If we consider the detail of the charge oscillations (Tab. I), we can see that they are almost only due to p electrons and especially to 7π electrons, as could be expected from the filling of the π band explained in I (Sect. 3.3.1.1). Moreover some similar phenomena of charge oscillations are well known and very important in the case of alternant hydrocarbons [6]. Here we are in a case very close to such hydrocarbons.

3.2 CHAINS WITH 2 FLUORINE ATOMS. — Figure 4 shows the fundamental difference between the 2 types of isomers. For the symmetrical chains
(middle part of Fig. 4), everything happens as if we had oscillations only at both ends of the chain on the
2 impurities, with immediate damping down towards the inside of it. The 2 terminal F atoms carry an
electron excess as can be expected from what we
wrote in I (Sect. 3.4.2.1) about the filling of the
« crystal » bands. Strictly speaking, we do not find
then any charge oscillations through the chain and
besides, the result seems to be independent of the n
parity.

Fig. 4. — Oscillations of charge Q (in electron number)
on the atoms in the F2Cn and FCnF (n = 3-5) chains
computed in CNDO.

On the other hand, the disymmetrical isomers are
very interesting. In the linear case (left part of
Fig. 4), they show very strong charge oscillations
along the chain, though more pronounced for odd n
(the case of the relatively stabler aggregates) than
for even n. In table II we see that the oscillations
essentially arise still from p electrons for both
F2C5 and F2C6. However they actually are very
important for F2C5, that is for odd-n clusters.

In another way, both ends of the chain, for odd n,
carry charges of different signs, with a very pro-
nounced excess on the terminal atom F1. This fact
seems to agree with the existence of a F2
« molecule » carrying a large negative charge and
which is bound to a Cn chain. As a result, the
Cn chain has a lack of electrons, therefore an sp band
less than half-filled and finally a lack of charge
(Q > 0) on the terminal C atom at the other end of
the chain. When n is even, the charge configurations
are quite different for n = 4 and 6, so we cannot
draw a general conclusion. We can simply notice
that, for F2C6, the values of Q on F1, F2 and
C1 are especially weak.

For the non linear isomers (right part of Fig. 4),
the oscillations are still very strong, but there is no
reversal for even n as in the linear F2Cn. Besides,
there is no periodicity of the charge oscillations for
even n, contrary to the odd n case where the
oscillations are consistent with the atomic positions
along the chain.

4. Conclusion.

In this paper, we have seen that the CNDO method
leads to interesting results on the charge distributions
in the linear F2Cn clusters and besides that the linear
chain model is a good tool to study this kind of
clusters.

For the FCn chains, the charges show « regular »
oscillations consistent with the atomic positions
along the chain, only when n is odd, that is in the
case of larger stabilities according to the results
reported in I. Moreover, the calculation shows, as
could be expected, a very important sp hybridization
on the adjacent F and C atoms, with a strong π
electron-acceptor character on the fluorine whatever
the n parity.

For the chains with 2 F atoms, the symmetrical
isomers give very weak oscillations which are inde-
dependent of the n parity. On the contrary, very large
charge oscillations appear on the disymmetrical
isomers and the sign of the charge on the terminal
atoms strongly depends on the n parity (linear
isomers). In the non linear isomer case, there is
always an excess of charge on the terminal atoms,
but one can observe regular oscillations of the
charges through the chain consistent with the atomic
positions only for odd n (that is in the case of larger
stabilities of the clusters).

Finally the calculation lets us conclude that
F2Cn clusters are likely to be built, as could be
anticipated, with an F2 molecule bound to a
Cn chain, which points out that the very strong F
electronegativity plays a fundamental role.

In the two cases, FCn and F2Cn, the oscillations are
almost exclusively due to π electrons, and this is a
good confirmation of the fact that it is the filling of
HOMO which governs the electronic properties of
the chains. Finally an important result is the conver-
gence between the large (resp. weak) stabilities of the
chains and the existence (resp. absence) of charge
oscillations commensurable with the « crystal »
periodicity.

Acknowledgments.

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Centre Inter Régional de Calcul Electronique
(C.I.R.C.E.) of the C.N.R.S. at the Université
Paris XI, Orsay.
References