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AB INITIO STRUCTURE OF GRAPHITE MONOFLUORIDE $(CF)_n$

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Abstract Using the Density Functional Theory formalism, we examined the structure of graphite monofluoride $(CF)_n$ where two conformations (chair and boat) were found to be experimentally possible. The chair structure is found to be energetically favoured with respect to the boat one by 0.145 eV per CF unit with a transition barrier estimated to be 2.72 eV. We conclude that the synthetized material could depend on the kinetics of the intercalation or could be a mix of both conformations.

INTRODUCTION

Fluorination of graphite[1] leads to the production of polycarbon monofluoride, $(CF)_n$, commonly known as graphite monofluoride, one of the most stable polymeric fluorocarbons, an exceptional lubricant under the extreme conditions of high temperature and high vacuum and a successful cathodic depolarizer in high-energy density battery.
Unfortunately, the layered $(CF)_n$ structure is still not really established. Derived from graphite by insertion of covalently bonded fluorine atoms above and below every hexagon of the carbon layers, the structure is composed of disrupt aromatic networks of graphite derivatives in which single carbon sheets are buckled rather than planar. Some doubt still subsists in the way these carbon layers are puckered (Figure 1).
The Rüdorff structure[2] is an infinite array of trans-linked cyclohexane chairs while an other geometrical possibility is an infinite array of cis-trans-linked cyclohexane boats[3]. X-ray powder diffraction studies[3] are in agreement with the chair structure indicating an hexagonal crystal lattice ($P6_3mc$, 2F+2C in the unit cell) while NMR second moment

measurements[4] favors the boat structure which results in an orthorhombic crystal lattice (Pmm2, 4F+4C in the unit cell). These two conformations are covalent compounds containing tetrahedrally coordinated sp^3 hybridized carbon atoms.

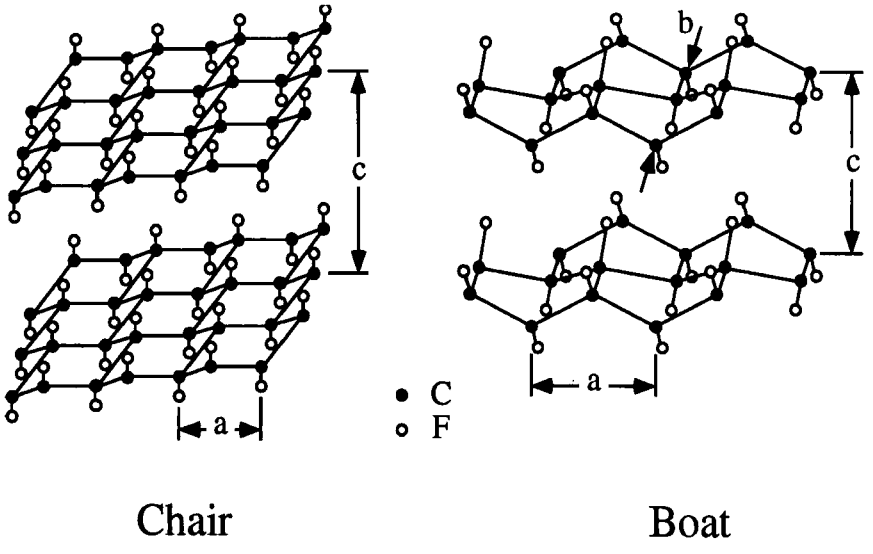

FIGURE 1 Structure of graphite monofluoride $(CF)_n$ in its two conformations. Carbon atoms are represented by black dots and fluorine atoms by white dots. In the chair conformation, a and c refer to the hexagonal unit cell axes. In the boat conformation, a, b and c refer to the orthorhombic unit cell axes.

THEORETICAL METHOD

As described in a more complete work[5], the Density Functional Theory[6] (DFT) has been implemented within the Local Density Approximation[7] (LDA) using the conjugate gradient algorithm[8]. The atomic potentials plus core electrons of carbon and fluorine have been replaced by extended norm-conserving separable *ab initio* pseudopotentials[9]. The discrepancies on total energy calculation due to the finite set of special k points used to sample the Brillouin zone are respectively 0.013 eV/atom (4 k points) in the chair conformation and 0.009 eV/atom (5 k points) in the boat one. Around a kinetic energy cutoff of 35 Ha, the calculated error on the total energy due to the finitness of the plane waves set, is ±0.04 eV/atom in both conformations.

The structural optimization study of graphite monofluoride has been carried out starting with planar carbon networks and relaxing the structure according to the Helmann-Feynman forces theorem. The different crystalline parameters have been considered

accurate enough when the residual forces on the atoms was inferior to 10^{-5} Ha/bohr. The Pulay correction[10] has been added to the total energy in order to decrease the error due to the use of different sets of plane waves.

AB INITIO STRUCTURES

The structural study has been limited to the AAA-stacking (each carbon atom have a corresponding atom in the plane directly above and below) which should not affect the intraplanar structure, principal interest of this work.

The *ab initio* results for the crystalline parameters of both conformations and the corresponding formation energies are shown in Table I.

Although in the chair conformation, there is only one kind of C-C bond (between two carbon atoms that bind with fluorine atoms on different sides of the graphitic plane) whose value is 1.552Å, in the boat conformation, two kinds of C-C bonds (between two carbon atoms that bind with fluorine atoms on different sides of the graphitic plane, or that bind with fluorine atoms on the same side of the graphitic plane) exist : 1.543Å and 1.625Å, respectively. This latter value is larger than the two others, likely due to the steric factor. The C-F bond length (1.37Å) is nearly identical in both structure.

Our theoretical results confirm that graphite monofluoride is geometrically different than other intercalated compounds and also "carbon-fluorine compounds" where graphene sheets are not distorted.

The formation energies of the two conformations (-10.66 eV per CF unit) are relative to the following chemical reaction : F_2 + graphite <—> 2 F(graphite).

A comparison of these values with experimental data (cfr. Table I) exhibits the well-known problem of overestimation of the cohesive energy (and formation energy) by the DFT. As this overestimation of the cohesive energy is very large, it may also indicate that the experimental samples do not closely conform to the structures that have been investigated in this study.

TABLE I. Values of crystalline parameters, carbon-carbon and carbon-fluorine bond lengths (in Å), angles (°), atomic positions (reduced coordinates) and formation energy relative to the F_2 molecule and solid graphite (in eV/CF unit) for the two conformations of graphite monofluoride $(CF)_n$. The first column contains the *ab initio* results while following ones are collections of best experimental evaluations relative to hypothetical $(CF)_n$ conformations.

$(CF)_n$	theory		experiment		
Chair					
Hexagonal unit cell					
a = b	2.553		2.53[11]	2.54[12]	2.57[13]
c	5.666		5.76[11]	5.80[12]	5.85[13]
Atomic positions					
C	(1/3, 1/3, -z)				
C	(2/3, 2/3, z)				
F	(1/3, 1/3, -u)				
F	(2/3, 2/3, u)				
with z=0.04273 and u=0.28452					
Bond lengths and angles					
C-C	1.552		1.47[11]	1.54[12]	1.53[13]
C-F	1.37		1.41[11]	1.39[12]	1.41[13]
C-C-C	110.7		118.8[11]		109.3[13]
C-C-F	108.2				
Formation Energy					
	-10.6603		-7.65[14]		
Boat					
Orthorhombic unit cell					
a	4.511		5.13[3]	4.11[15]	
b	2.527		2.51[3]	2.47[15]	
c	5.673		6.16[3]	5.76[15]	
Atomic positions					
C	(x, 1/2, z)				
C	(1/2-x, 0, -z)				
C	(1/2+x, 0, -z)				
C	(-x, 1/2, z)				
F	(1/4-w, 1/2, u)				
F	(1/4+w, 0, -u)				
F	(3/4-w, 0, -u)				
F	(3/4+w, 1/2, u)				
with x=0.18012, z=0.05492, w=0.00284 and u=0.28943					
Bond lengths and angles					
C-C	1.543	1.625	1.54[3]		
C-F	1.364		1.40[3]	1.64[15]	
C-C-C	114.1	109.9			
C-C-F	107.7	102.8			
Formation Energy					
	-10.5155		-7.65[14]		

The energetic difference between these two structures is 0.0725 eV/atom (in absolute value) in favour of the chair conformation. Even if this structure is energetically the most favourable, kinetic factors may govern the actual synthesis. In order to test this possibility, the potential barrier needed to transform the boat in the chair structure has been estimated by exchanging the positions of two fluorine atoms (concerted exchange) which generates one possible transition path using a linear combination of the extreme atomic positions of the two states. The *ab initio* energy barrier of this path is 2.72 eV and must be considered as a maximal height for the potential barrier.

The actual transition path is likely different from our simple linear combination of positions. The error was estimated by relaxing the atomic coordinates at the top of the linear transition path, using the forces acting on the atoms in that geometry. This procedure only decreased the height by 0.106 eV, with residual forces (max: 0.01 Ha/bohr) five times smaller than the ones observed at the top of the linear transition path. We conclude from that transition path study, that the boat conformation is a metastable one, separated from the chair conformation by a large energy barrier.

CONCLUSION

The graphite monofluoride $(CF)_n$ has been characterized using first-principles techniques. As a result of that investigation, we have found three important energetic quantity : the formation energy (about 10.5 eV per CF in theory, 7.65 eV from experiment), the energy difference between the boat and chair conformations (0.145 eV per CF) and the energy barrier between the boat and chair conformations (2.72 eV for the linear concerted exchange of two F atoms). Although the chair conformation is the most stable one, the energy barrier is rather large, and we think that the material that is synthetized could depend on the condition of the synthesis. Indeed, the boat conformation material is metastable, but the formation energy is large enough to overcome the energy barrier, and a simulation of the intercalation process using molecular dynamics would be very interesting. In the final product, some disorder in the repartition of the alternation of C-F below and above the plane could be present, as well as islands of boat conformation in a mostly chair conformation material. On the other hand, the steric factor could prevent the kinetic formation of the boat conformation as well. These further issues are still difficult to address by nowadays *ab initio* methods, and will be left for future studies.

In any case, we advise experimentalists to pay attention to the way their material has been synthetized, and not to assume a well-defined, unique, structure of CF.

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