

Heteronuclear dipolar recoupling using Hartmann–Hahn cross polarization: A probe for ^{19}F – ^{13}C distance determination of fluorinated carbon materials

Jérôme Giraudet^a, Marc Dubois^b, Katia Guérin^b, Céline Delabarre^b, Pascal Pirotte^a,
André Hamwi^b, Francis Masin^{a,*}

^a*Matière Condensée et Résonance Magnétique, Université Libre de Bruxelles (U.L.B.), CP 223, Boulevard du Triomphe, B-1050 Bruxelles, Belgium*

^b*Laboratoire des Matériaux Inorganiques, UMR CNRS 6002, Université Blaise Pascal, 24 av. des Landais, 63177 Aubière Cedex, France*

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Abstract

A NMR determination of the C–F bond length in fluorinated carbon materials using dipolar recoupling is described. To this end Hartmann–Hahn cross polarization with magic angle spinning (inverse cross polarization sequence) is used. A description of the corresponding ^{13}C magnetization evolution as a function of the evolution time and its simulation for typical fluorinated samples are realized.

The procedure is applied to 15 different materials having different bonding (semi-covalent or covalent) and from various carbon allotropic varieties. The distance evolves from 0.138 ± 0.002 nm for covalent bonding to 0.1445 ± 0.002 nm for semi-covalent bonding. Other parameters may affect the C–F bond length e.g. steric hindrance which leads for fluorinated fullerenes to an increase of this distance up to 0.146 ± 0.002 nm.

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1. Introduction

Fluorination of carbon materials such as polymers [1–3], graphite [4–6], fullerenes [7–10] or nanofibres [11,12] have been the focus of a great number of studies because of their various applications, for example solid lubricants [13,14] or cathode material in high energy density lithium batteries [6,15–17]. Several temperatures and fluorination techniques can be used: fluorination with fluorine gas in presence (or not) of traces of metal fluorides or HF as catalyst, fluorination with a gaseous mixture MF_n , HF and F_2 ($\text{MF}_n = \text{IF}_5$, BF_3 , ClF_x, \dots), use of chemical agent (BrF_3 , MnF_3 , NiF_3 , CoF_3, \dots), etc.

Graphite fluorides $(\text{C}_2\text{F})_n$ and $(\text{CF})_n$, prepared at 350 and 600 °C, respectively, possess a covalent C–F bond [5].

From neutron diffraction data, the C–F bond length of both materials was determined to be 0.136 nm [18]. On the other hand, at room temperature with a gaseous mixture of MF_n , HF and F_2 ($\text{MF}_n = \text{IF}_5$, BF_3 , ClF_x, \dots), semi-covalent carbon fluorides $\text{CF}(\text{MF}_n)$ are obtained exhibiting similarities with graphite intercalation compounds. The bonding progressively changes from semi-covalent to a mainly covalent character at a fluorination post-treatment temperature close to 450 °C [19–22]; in addition a new hybrid structure with both semi-covalent and covalent characters is formed in the intermediate temperature range (close to 350 °C) [19,20]. During the electrochemical discharge in primary lithium batteries, the C–F bonds are broken via the formation of LiF. The discharge potential of a graphite fluoride electrode depends on the C–F bonding and is weaker when the C–F bonding is covalent [5,6]. Progressive reinforcement of the C–F bonding covalency during the post-treatment of the room temperature graphite fluorides, whatever the used catalyst, results in a

*Corresponding author. Fax: +32 2 650 5675.

E-mail addresses: jerome.giraudet@ulb.ac.be (J. Giraudet),
fmassin@ulb.ac.be (F. Masin).

decrease in the discharge potential. Simultaneously, this post-treatment induces an additional fluorination, increasing the fluorine content, which is available for the electrochemical process. The specific capacity is then improved. The electrochemical performances of the hybrid materials post-treated between 400 and 500 °C are interesting, particularly considering the energy density. Thanks to the coexistence of two types of carbon atoms, sp^2 and sp^3 hybridized, the electrochemical properties of these post-fluorinated materials are then tuneable by adjusting the treatment temperature. The control of the sp^2 and sp^3 carbon atoms ratio by the post-treatment allows the adjustment of the capacity–discharge potential couple as a function of the required application in lithium batteries.

Fluorinated fullerenes are obtained with a wide range of composition, from $C_{60}F_2$ [9] to $C_{60}F_{60}$ [7]. The experimental conditions (time and temperature of reaction, mode of fluorination, etc.) determine these variations in C/F ratio. For $C_{60}F_{48}$, both X-ray diffraction and DFT calculation indicated a C–F bond length in the range 0.136–0.140 nm [10]. Another study from Kniaz et al. [7] has shown an X-ray C–F bond length of 0.149 nm for $C_{60}F_{35-44}$.

The C–F bond length of fluorinated carbons appears as a good indication of the C–F bonding i.e. covalence. A C–F bond length reduction is expected when the covalence increases. Together with other experimental methods, the C–F bond length can be estimated by nuclear magnetic resonance because this length is included in the expression of the dipolar interaction which can be determined using dipolar recoupling techniques such as rotational echo double resonance (REDOR) [23] or transferred echo double resonance (TEDOR) [24,25]. Although the dipolar coupling information is lost when Hartmann–Hahn cross polarization (CP) associated to magic angle spinning (MAS) is used it can be reintroduced into the spectrum thanks to the inverse cross polarization (ICP) sequence (Fig. 1). In comparison with the REDOR sequence usually used for the internuclear distance measurements, the ICP sequence required easier experimental adjustment, the

main difficulty is the Hartmann–Hahn matching. A second advantage is the absence of rotor-synchronized π pulses in ICP sequence unlike the REDOR sequence. Indeed, for the REDOR sequence and at high spinning speed the finite pulse length could result in an artefact. At high speed the π pulse then represent a significant fraction of the rotor period. This method was successfully applied to $(CF)_n$ and $(C_2F)_n$ types graphite fluorides [26,27]. In both cases, a C–F bond length of 0.138 ± 0.002 nm was found in accordance with the value recently obtained from neutron diffraction data (0.136 nm) [18].

In this paper, we extrapolated this method to a wide range of fluorinated carbons: molecular monomer (chlorotrifluoroethylene, CTFE), one-dimensional fluorinated polymer (polytetrafluoroethylene, PTFE) and bi-dimensional materials: semi-covalent room temperature graphite fluorides $(C_4F)_n$ and samples obtained after their post-fluorination (various post-treatment temperatures were applied). This treatment allows a progressive conversion of the semi-covalent starting material into covalent. In addition, nanomaterials were also studied such as carbon nanofibres (CNFs) fluorinated at various temperatures and fluorinated fullerenes giving an example of tri-dimensional material. A panel of 15 different fluorinated carbons was studied and their C–F bond length determined.

2. Materials and methods

2.1. Preparation of the samples

Polytetrafluoroethylene (PTFE; $[-CF_2-]_n$) and chlorotrifluoroethylene (CTFE; $CF_2 = CFCl$) were commercial products (Aldrich and Solvay, respectively).

$(C_2F)_n$ and $(CF)_n$ were synthesized using the conventional method: a monel boat containing carbon was placed in a nickel reactor and heated to 380 and 600 °C under pure F_2 gas flow for $(C_2F)_n$ and $(CF)_n$, respectively (Table 1).

Hybrid structure graphite fluoride was obtained by a two steps process. First, the reaction at room temperature of graphite with a gaseous mixture of HF, F_2 and IF_5 (the experimental conditions had been already published elsewhere [28]); secondly, a post-fluorination at 350 °C. This sample was denoted as CF(IF_5)-350. A re-fluorination at 530 °C leads to a sample similar to $(CF)_n$ and named CF(IF_5)-530.

$(C_4F)_n$ type graphite fluoride was prepared by fluorination of graphite at room temperature using a gaseous mixture of F_2 , HF (obtained from heated KHF_2), and catalytic chloride species ClF_x ($x = 3$ mostly; a few ClF_5 can also be formed due to the excess of F_2) obtained by heated KCl under F_2 . Although ClF_x was used as catalyst, no chlorine species are intercalated in the resulting sample [22]. Then, the compound was treated under one atmosphere of pure fluorine gas at various temperatures i.e. 350, 450 and 550 °C and new samples named $(C_4F)_n$ -350, $(C_4F)_n$ -450 and $(C_4F)_n$ -550 are obtained.

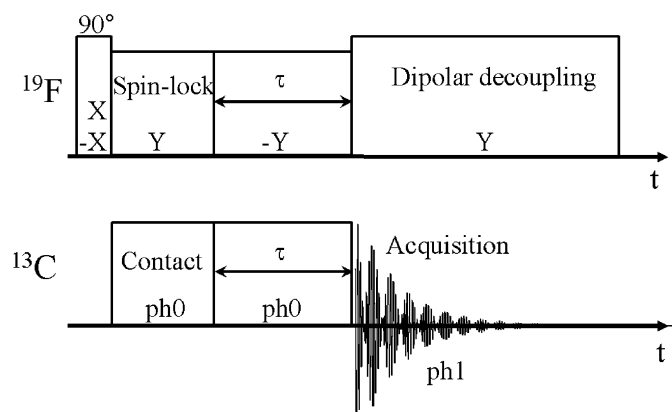


Fig. 1. Schematic diagram of the inverse cross polarization sequence. The evolution time is τ . The phase list ph0 and ph1 are $(X X Y Y - X - X - Y - Y)$ and $(X - X Y - Y - X X - Y Y)$, respectively.

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