

## The Solid State $^{13}\text{C}$ -NMR and $^{19}\text{F}$ -NMR Spectra of Some Graphite Fluorides

CHARLES A. WILKIE, GONG-YU LIN, AND DANIEL T. HAWORTH

*Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233*

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The solid state  $^{13}\text{C}$  nuclear magnetic resonance spectra of fluorinated graphites show two resonances, one of which is assigned to aromatic carbon and the other to aliphatic carbon. The resonances are very broad with the high-field resonance centered at about 35 ppm below tetramethylsilane (TMS) and a low-field resonance centered at about 160 ppm below tetramethylsilane. The high-field resonance is typical of an  $sp^3$ -like carbon and the low-field resonance is assigned to  $sp^2$ -like carbons. It is found that the aromatic resonance in graphite decreases with an increase in fluorination of the graphite fluorides examined in this study. The  $^{19}\text{F}$  nuclear magnetic resonance spectra of  $\text{C}_4\text{F}$  and  $\text{CF}_1$  each show one resonance. The fluorine resonance in  $\text{C}_4\text{F}$  is 180 ppm above  $\text{CFCl}_3$  whereas the fluorine resonance in  $\text{CF}_1$  is 55 ppm above  $\text{CFCl}_3$ . These peaks are in the range for fluorine bonded to aromatic and aliphatic carbons, respectively.

### Introduction

The study of solid state materials by carbon-13 nuclear magnetic resonance (NMR) spectroscopy is a rapidly expanding area (1, 2). Materials ranging from fairly simple organic compounds, e.g., adamantane (3-5), to carbides (6), polymers (7), coals (8-14), and elemental carbons (diamond and graphite) (15, 16) have been reported. The spectra are normally broad and featureless unless special techniques such as cross-polarization (3) and high-speed rotation at the magic angle ( $54.7^\circ$ ) with dipolar decoupling (17) are utilized.

The spectra of model compounds, e.g., adamantane, have provided the necessary background for interpreting the more complex materials. Two resonances have been observed and assigned in coals to the aromatic and aliphatic carbon atoms (8-14). In graphite and diamond (16) again two resonances are usually observed. The prin-

cipal resonance in graphite occurs at about 170 ppm below TMS in a typical aromatic resonance position. The minor resonance, about 50 ppm above TMS, is quite variable. In highly graphitized graphite this resonance is usually not present, whereas in other graphite samples it seemingly makes a large contribution. A similar situation occurs for diamonds; the major resonance is now the upfield peak, the minor resonance the downfield peak. Both of these resonances are at essentially the same positions as observed in graphite, and these resonances vary in intensity depending on diamond quality. Only the high-field resonance is observed in the best-quality diamond.

### Experimental

The  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were obtained on a JOEL-FX60Q spectrometer operating in the external lock mode. A flip angle of about  $30^\circ$  was used. TMS ( $^{13}\text{C}$ ) and

$\text{CFCl}_3$  ( $^{19}\text{F}$ ) were used as external references by tube substitution before and after a spectrum was recorded. The spectra were obtained using 8192 data points collected over a sweep width of 10 000 Hz. A scan repetition rate of 0.6 sec ( $^{13}\text{C}$ ) and 2.0 sec ( $^{19}\text{F}$ ) was used and the spectra were obtained after accumulation of about 100 000 pulses ( $^{13}\text{C}$ ) and 16 000 pulses ( $^{19}\text{F}$ ). The samples were packed into a 10-mm ( $^{13}\text{C}$ ) or 5-mm ( $^{19}\text{F}$ ) NMR tube and the spectrum was obtained directly. The graphite fluoride samples (Fluorographite) were obtained from the Ozark-Mahoning Company. They are all powders of size 0.5 to 5  $\mu\text{m}$  which vary in color depending on the degree of fluorination. Fluorine analysis was done by  $\text{Na}_2\text{CO}_3$  fusion, then a Willard-Winter distillation followed by  $\text{Th}(\text{NO}_3)_4$  titration (18).  $(\text{CF}_1)_x$  prepared from graphite gives  $d$ -spacings of 1.30, 2.23, and 6.06  $\text{\AA}$  whereas preparation from carbon black shows  $d$ -spacings of 1.32, 2.22, and 6.7  $\text{\AA}$ . Graphite fluorides having more than 50% (w/w) fluorine have a similar diffraction pattern whereas low-fluorine-containing samples show a diffraction pattern like that of a graphite (18).

## Results and Discussion

The  $^{13}\text{C}$  NMR spectra of eight different samples of fluorinated graphites were obtained. Various degrees of fluorination were represented, the general formula being  $(\text{CF}_x)_n$  where  $x$  is 0.23, 0.39, 0.49, 0.60, 0.71, 0.94, 1.0, and 1.12 by analysis. The stoichiometric sample  $\text{CF}_1$  indicates a completely aliphatic structure with every carbon bearing one fluorine (19). The excess fluorine sample,  $\text{CF}_{1.12}$ , is again completely aliphatic with a significant concentration of  $\text{CF}_2$  groups at the edges of the layers (20). All other samples indicate partial fluorination of the graphite structure and therefore only partial breakdown of the aromatic character of the graphite. Only two stoichiometric graphite fluorides are known,  $\text{CF}_1$

and  $\text{C}_4\text{F}$  (21), although a third compound,  $\text{C}_2\text{F}$ , has been recently reported by Watanake (22). Presumably  $\text{CF}_{0.23}$  is essentially only  $\text{C}_4\text{F}$ , while  $\text{CF}_1$  is also a pure phase as is perhaps  $\text{CF}_{0.49}$ . All other values of  $x$  must represent various amounts of these pure phases.

The chemical properties of these graphite fluorides have not been fully studied; however, fluorinated graphite powders in the range of  $\text{CF}_{0.5}$  to  $\text{CF}_{1.0}$  are used in the construction of positive electrodes for nonaqueous high-energy batteries (23) and various fluorinated graphites have been used as lubricants or lubricant powders (for example, see (24)). The graphite fluoride polymers  $(\text{CF}_x)_n$  used in these experiments have been characterized by colors which range from black ( $x = 0.25$ ) to grey ( $x = 0.8$ ) to white ( $x = 1.12$ ) powders. These polymers are all fine hydrophobic powders which are insoluble in water and common organic solvents. Their lubricity and conductivity depends on the degree of fluorination (25). An X-ray photoelectron spectroscopy (XPS) study of graphite monofluoride has shown a strong mixing of the carbon and fluorine orbitals (26).

The  $^{13}\text{C}$  NMR spectra of these samples may be divided into two classes based on the number of observable resonances. In all samples where the fluorine to carbon ratio is less than one, two peaks, at approximately 160 and 35 ppm below TMS, respectively, are observed. The bandwidths at half-height are approximately 1 kHz. The low-field resonance is in essentially the same position as observed in graphite and therefore represents the aromatic carbons ( $sp^2$ ) in the sample. The high-field resonance is about 100 ppm to lower field than the diamond resonance which probably reflects the influence of fluorine on the resonance. It is assigned to the aliphatic carbon ( $sp^3$ ) atoms. Support for these assignments comes from the observation that the aliphatic resonance grows relative to the downfield aromatic

resonance as the degree of fluorination increases.

The other two materials,  $\text{CF}_1$  and  $\text{CF}_{1.12}$ , both exhibit only the upfield resonance. This is assigned to the aliphatic carbons which is in perfect accord with what is known of these materials. Typical spectra for  $\text{C}_4\text{F}$  and  $\text{CF}_1$  are given in Figs. 1 and 2, respectively.

The fluorine-19 NMR spectra gives further credence to these assignments. In  $\text{C}_4\text{F}$  one resonance is observed at 180 ppm above  $\text{CFCl}_3$  while in  $\text{CF}_1$  a single resonance is observed at 55 ppm above  $\text{CFCl}_3$ . Fluorine bonded to an aromatic carbon shows a more upfield resonance than does fluorine bonded to an aliphatic carbon, e.g.,  $\text{C}_6\text{F}_6$ , -162.9 ppm;  $\text{C}_6\text{H}_5\text{CF}_3$ , -63.9 ppm;  $\text{CF}_3\text{COOH}$ , -78.5 ppm (27). The  $^{19}\text{F}$  resonance in  $\text{CF}_1$  is quite reasonably assigned as indicating aliphatic carbon-fluorine bonds while the resonance of  $\text{C}_4\text{F}$  indicates aromatic carbon-fluorine bonds.

The electrical conductivity of  $\text{C}_4\text{F}$  is roughly two powers of 10 less than graphite. The chemical shift for fluorine in  $\text{C}_4\text{F}$  indicates that fluorine must be affected by the ring current in the aromatic system.

### Conclusions

The  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra of graphite fluorides may be used to distinguish between aromatic-type and aliphatic-type materials. Due to the combination of relaxation and saturation effects the intensities do not give a true indication of the amount of a particular structural type. However, this may be accomplished through the utilization of some of the newer techniques of resolution enhancement (1, 2, 4). There is a real possibility that one may be able to quantitatively determine the types and amounts of carbon atoms in a variety of insoluble carbon-containing materials. We are actively pursuing this possibility.

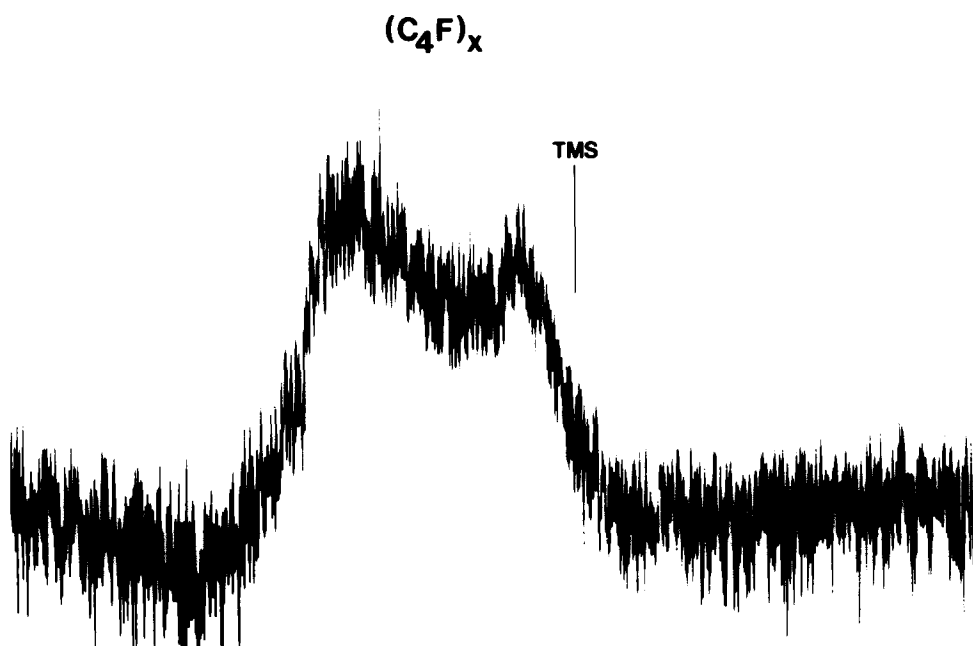


FIG. 1.  $^{13}\text{C}$  NMR spectrum of  $(\text{C}_4\text{F})_x$ . The total spectral width is 10 000 Hz and the resonances are approximately 160 and 41 ppm from TMS.

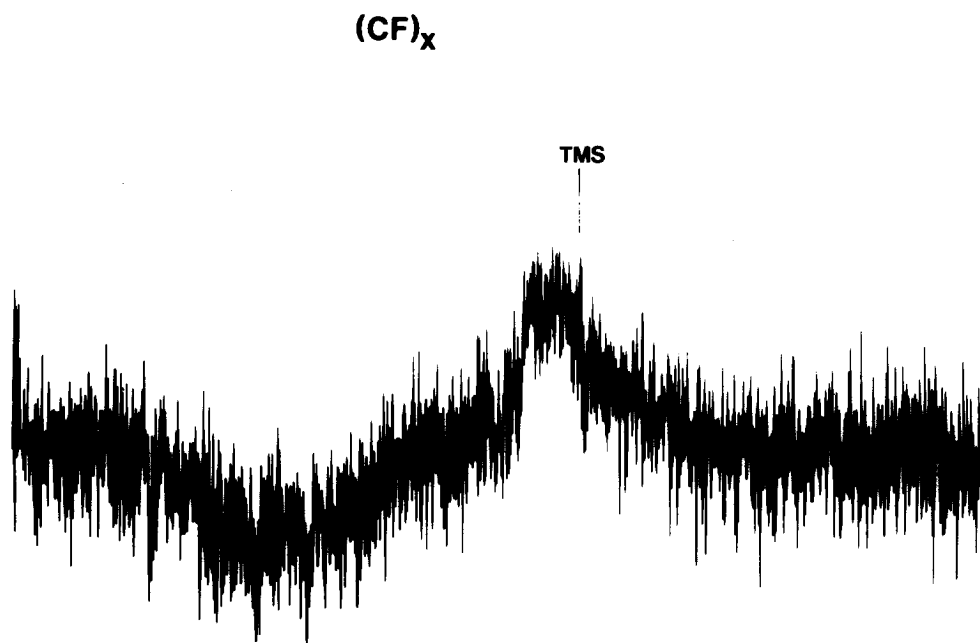


FIG. 2. <sup>13</sup>C NMR spectrum (CF)<sub>x</sub>. The total spectral width is 10 000 Hz and the major resonance is approximately 21 ppm downfield from TMS.

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