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RAMAN, INFRARED, AND N.M.R. STUDIES OF THE GRAPHITE HYDROFLUORIDES C_xF_{1-δ}(HF)_δ (2 ≤ x ≤ 5)

T. Mallouk, B.L. Hawkins, M.P. Conrad, K. Zilm, G.E. Maciel, and N. Bartlett

June 1984

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RAMAN, INFRARED, AND N.M.R. STUDIES OF THE
GRAPHITE HYDROFLUORIDES \( C_{x} F_{1-\delta}(HF)_{\delta} \) (2 \( \leq x \leq 5 \))

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Abstract

Raman spectra of $C_{x}F_{1-\delta}(\text{HF})_{\delta}$ ($x/\delta \approx 12$) show bands at 1600, 1355 and 839 cm$^{-1}$, which are attributed to graphite-like vibrational modes of the carbon atom sheets. The infrared spectra show, in addition to graphite-like bands, absorptions at 1270 and 1100 cm$^{-1}$ which are attributed to C - F stretching. Variable contact time CP-MAS $^{13}$C n.m.r. spectra have been obtained for $x = 2.05$ and 3.70. In both spectra, two peaks (+135 and +88 ppm, rel. TMS) are seen, which are attributed, respectively, to graphitic and C - F carbons. The ratio of graphitic to C - F carbon atoms has been found to be 1.6(2):1 in $C_{2.05}F_{0.82}(\text{HF})_{0.18}$. The carbon atom sheets in $C_{x}F_{1-\delta}(\text{HF})_{\delta}$ appear to be very similar to those in pristine graphite. The bonding of fluorine to carbon is highly ionic. Bonding models are discussed.

1. Introduction

It is well known that graphite and neat fluorine gas do not interact at room temperature and ordinary pressures. At higher temperatures (380 - 600°C), the lamellar compounds $(C_{2}F)_{n}$ and $(CF)_{n}$ are formed, in which the carbon atoms are disposed in puckered sheets [Rudorff & Rudorff, Z. Anorg. Allgem. Chem. 1947, Kita et al. 1979]. In the presence of HF, graphite is spontaneously intercalated by fluorine, at room temperature. The first accounts [Rudorff & Rudorff, Chem. Ber. 1947b] of such a reaction describe the first stage compounds $C_{x}F_{1-\delta}(\text{HF})_{\delta}$, where $3.57 < x < 4.03$ and $\delta$ is assumed to be small. Later studies [Lagow et al. 1972, 1974] have shown that $\delta$ is indeed appreciable (0.27 - 0.34). In our preliminary studies of this system [Mallouk & Bartlett 1983], we reported the
compositions \( C_x F (2.0 \leq x \leq 5 - 6) \). Analysis specifically for HF content has established that these compounds contain approximately one hydrogen atom for every twelve carbon atoms, and are better represented as
\[ C_x F_{1-\delta}(HF)_{\delta} \] (where \( \delta \approx 1/12x \)).

The structure of "tetracarbon monofluoride" (C\(_4\)F) has been discussed by Rudorff and Rudorff [Chem. Ber. 1947b, 1959]. While it cannot be unequivocally demonstrated from their X-ray powder diffraction data, they proposed that in C\(_4\)F the carbon atom sheets were flat and that the fluorine atoms made close (~1.4 Å) contacts to the carbons. Their finding of high electrical conductivity for C\(_4\)F\(_{1-\delta}(HF)_{\delta}\) also supported their notion that the carbon atom sheets were planar. Recent work in these laboratories [Mallouk & Bartlett 1983, Mallouk 1983] has established that chemical fluorination of graphite, to compositions \( C_x F_{1-\delta}(HF)_{\delta} \), \( x > 2.3 \), may be reversed entirely (to graphite) by electrochemical means. This reversibility is also consistent with the carbon atom array not being very much distorted away from planarity by fluorination.

The vibrational spectra presented here for \( C_x F_{1-\delta}(HF)_{\delta} \), together with CP-MAS \(^{13}\)C n.m.r. spectra, establish that the carbon sheets are indeed planar, even in the limit \( x \approx 2 \), where the compound is an electrical insulator. These spectra also indicate that the binding of fluorine to carbon is the same throughout the entire range of composition; fluorine atoms are found to be attached singly to carbon atoms via weak, semi-ionic bonds. The Raman spectra establish that the domains of fluorine atom ordering in the \( ab \) plane are about 50 - 100 Å in extent. \(^1\)H n.m.r. spectra have shown that the proton containing species within the graphite binds to the host lattice. Motion or exchange of that species is slow at 298° K.
2. Experimental

(a) Preparation

\( C_{x}F_{1-\delta}(HF)_{\delta} \) was prepared by reaction, at 20°C, of graphite powder (Union Carbide SP-1) with \( F_{2} \) (2 atm.) and gaseous HF (for \( x \geq 2.4 \)), and from graphite, \( F_{2} \) (2 atm.), and liquid HF (for \( x = 2.0 \)). The samples were pumped out for 24 hours at the conclusion of the reaction and elemental analyses for carbon and hydrogen were performed. The hydrogen was determined as HF by pyrolyzing ca. 100 mg. \( C_{x}F_{1-\delta}(HF)_{\delta} \) at 1000°C and condensing the volatiles into a trap containing KOH solution; potentiometric back-titration with HCl solution gave the hydrogen content. Typical compositions were: \( C_{2.05}F_{0.18} \) (C/H = 11.6), \( C_{2.70}F_{0.22} \) (C/H = 12.3), and \( C_{3.75}F_{0.33} \) (C/H = 11.4).

(b) Vibrational Spectra

Transmission infrared spectra of \( C_{2.5}F_{1-\delta}(HF)_{\delta} \) were recorded on a Nicolet 8000 HV F.T.-I.R spectrometer. The sample was prepared by grinding a graphite chip in such a way that the \( c \) - axis lay in the plane of the resulting thin flake. The flake was then intercalated by interaction with fluorine and HF vapor at 20°C. This arrangement exploits the high conductivity anisotropy of graphite and its compounds; electromagnetic radiation may be transmitted through the graphite flake provided its electric vector is aligned parallel to the \( c \) - axis. Normally, vibrational modes which have in-plane components are not observed. In \( C_{2.5}F_{1-\delta}(HF)_{\delta} \), however, the \( ab \) plane conductivity is low enough for all the infrared active modes to be seen.
Raman spectra were recorded on a J-Y Ramanor spectrometer, using argon ion laser (488.0 nm.) excitation, for several compositions of $C_x F_{1-\delta} (HF)_\delta$. The spectral resolution was 2 cm$^{-1}$. Typically, 100 scans were taken and added together, from powder samples which were contained in quartz X-ray capillaries; the quartz line at 808 cm$^{-1}$ provided a fiducial marker in the spectra.

(c) N.m.r. Spectra

$^{13}$C CP-MAS spectra of $C_{2.05} F_{1-\delta} (HF)_\delta$ and $C_{3.70} F_{1-\delta} (HF)_\delta$ were obtained using a modified Nicolet NT-150 spectrometer equipped with a home-built solids probe and associated high power pulse amplifiers and matching networks. The 150 MHz console proton decoupler was re-tuned and modified for operation at 141.2 MHz for $^{19}$F spin locking and decoupling. An Amplifier Research Model 200L amplifier operating at 100 watts was used as the final stage of the decoupler to provide a Hartmann-Hahn match of 50 kHz. Contact times were varied from 100 μsec to 20 msec with pulse repetition times of about 1 sec. Samples were spun at the magic angle in 10 mm. o.d. Delrin rotors at about 2.8 kHz. The $^{13}$C chemical shifts were referenced to the aromatic resonance of a solid hexamethyl benzene external standard, which was taken as 132.2 ppm. The $^1$H n.m.r. spectrum of $C_{2.15} F_{0.83} (HF)_{0.17}$ powder was recorded at 20°C on a home-built spectrometer operating at a proton resonance frequency of 360 MHz.

(d) X-Ray Powder Diffraction

Powder patterns were taken on a General Electric Precision Camera, 45 cm. circumference, using Ni-filtered CuK$_\alpha$ or Zr-filtered MoK$_\alpha$ radiation.
3. Results and Discussion

(a) Vibrational Spectra

The Raman spectra of powdered samples of $C_x F_{1-\delta}(HF)_\delta$ are shown in figure 1

Figure 1 here (for legend see p. 21)

for several values of x. The spectra are all virtually identical to the spectrum of graphite itself [Solin 1980], which has a Raman mode at 1581 and an infrared mode 848 cm$^{-1}$ corresponding, respectively, to in-plane and out-of-plane motions of the carbon atoms. In addition to these, a broad band at 1355 cm$^{-1}$ is observed. Such a band is seen in the Raman spectrum of graphite powder which is poorly ordered or which has been disordered by grinding. It has been attributed to a zone boundary mode which is Raman-inactive in crystallites of large extent [Tuinstra & Koenig 1970]; it corresponds to an in-plane ring-breathing motion. The intensity of this band relative to the graphite $E_{2g}$-like band at 1600 cm$^{-1}$ indicates the extent of the ordered domains in the ab plane [Tuinstra & Koenig 1970]. The domain size, in the case of $C_x F_{1-\delta}(HF)_\delta$ is in the range of 50 - 100 Å. A slight shifting ($\sim$ 30 cm$^{-1}$) towards lower frequency of the $\sim$1600 cm$^{-1}$ band is found for the highest fluorine concentrations, indicating a very slight weakening of the carbon to carbon bonding; this observation is in accord with the small increase in bond distance (by .006 Å) inferred from the crystallographic a-spacings [Mallouk & Bartlett 1983], for compositions in which the C/F ratio is nearly two. The intensity of the C - F stretching band is expected to be low in the Raman. It is barely discernable, near 1100 cm$^{-1}$.

The transmission infrared spectrum of $C_{2.5} F_{1-\delta}(HF)_\delta$ (figure 2) shows, in addition

Figure 2 here (for legend see p. 21)
to the graphite-like bands situated at 1587 and 850 cm\(^{-1}\), an exceptionally strong absorption at \(\sim 1100\) cm\(^{-1}\) and a shoulder at 1270 cm\(^{-1}\). Both are attributed to C - F stretching vibrations. Comparison of these with the C - F stretching frequencies in \((\text{CF})_n\) and \((\text{C}_2\text{F})_n\) (1219 and 1221 cm\(^{-1}\), respectively [Rudorff & Rudorff, Chem. Ber. 1947b]) suggests that for the bulk of fluorine in \(\text{C}_x\text{F}_{10-\delta}(\text{HF})_\delta\) (represented by the \(\sim 1100\) cm\(^{-1}\) band) the C - F bond order is lower than in the other carbon fluorides. The 1270 cm\(^{-1}\) band may arise from a small concentration of \(>\text{CF}_2\) groups at the edges of the carbon-atom layers.

The presence of graphite-like vibrations, occurring at practically the same frequency as in graphite itself, establishes the planarity of the carbon sheets in \(\text{C}_x\text{F}_{10-\delta}(\text{HF})_\delta\), even at C/F ratios of two.

(b) \(^{13}\text{C}\) n.m.r. Spectra

Magic angle spinning spectra of \(\text{C}_x\text{F}_{10-\delta}(\text{HF})_\delta\) powders were obtained, using \(^{19}\text{F} \leftrightarrow ^{13}\text{C}\) cross polarization, for \(x = 2.05\) and \(x = 3.70\). In both spectra (figure 3) two peaks, separated by 47 ppm, are observed, the similarity of the spectra suggesting the same bonding environments for both compounds.

The low field peak (\(\delta = 135\) ppm relative to TMS) exhibits spinning sidebands, displaced \(\pm 97\) ppm from the central peak, indicating a large chemical shift anisotropy for these carbon atoms. This chemical shift and shift anisotropy are characteristic of aromatic (i.e., graphite-like) carbon. The high field
peak is attributed to carbon atoms bound to fluorine. In addition, a small peak at 112 ppm has been resolved in some of the spectra. This peak is attributed to a small concentration of >CF$_2$-type carbon atoms. These are probably found at the edges of the grains.

The ratio of the aromatic and C - F carbons in the sample may be determined by varying the $^{19}$F - $^{13}$C cross polarization contact time. The spectral intensity arising from the $i$th carbon spins is given by [Mehring 1976]:

$$I_i = kN_i [1 - \frac{T_{1\rho}}{T_{1\rho}^i}]^{-1} [\exp(-t/T_{1\rho}) - \exp(-t/T_{1\rho}^i)]$$

Here $t$ is the contact time, $T_{1\rho}$ is the fluorine spin-lattice relaxation time in the rotating frame, $k$ is an instrumental constant, $N_i$ is the relative concentration of the $i$th spins, and $T_{1\rho}^i$ is the characteristic cross relaxation time which depends on the strength of the dipolar coupling (and hence the distance) between the $i$th carbon atoms and their fluorine atom nearest neighbors. The variable contact time spectrum of C$_2$O$^{0.82}$(HF)$_{0.18}$ is shown in figure 4. Note that the high-field peak is magnetized more quickly than the graphitic peak, indicating, for the high field nuclei, bound fluorine.

Table 1 shows the observed and calculated spectral intensities for C$_2$O$^{0.82}$(HF)$_{0.18}$ as a function of contact time. The C - F peak is fit...
quite well to a $T_{\text{CF}}$ of 0.10(2) msec and a fluorine $T_{1\rho}$ of 6.0(5) msec. For the graphitic peak, a satisfactory fit can only be obtained from the superposition of approximately equal concentrations of carbon spins with short (0.40(5) msec) and long (2.50(8) msec) values of $T_{\text{CF}}$. The relative concentration of the graphitic and C - F carbon atoms is found to be 1.6(2):1. This is in good agreement with the value expected (1.50), assuming that the HF present is not bound to carbon, and that only two-center C - F bonds are formed (and not three-center F - C - F bonds, as we had previously allowed as a plausible bonding model) [Mallouk & Bartlett 1983].

The $^{13}$C n.m.r. spectra are consistent with structures which, like Rudorff's [Rudorff & Rudorff 1947b, Rudorff 1959], allow for planar carbon-atom sheets and attachment of carbon to only one fluorine atom at a time. The persistence of graphitic carbon, even at C/F ratios approaching two, suggests that delocalized $\pi$-bonding is maintained in the carbon-atom sheets.

(c) The Role of HF in $C_x F_{1-\delta}(HF)_\delta$

The persistence of HF in first-stage graphite hydrofluorides is noteworthy. When $C_{2.05} F_{0.82}(HF)_{0.18}$ is heated to 140°C and subjected to a dynamic vacuum for two days, only about half of the HF is removed; the crystallographic $c$-spacing of the material so treated undergoes a contraction from 6.25(2) to 5.92(2) Å. The bulk of the remaining HF is not removed at temperatures below 300°C. When $C_x F_{1-\delta}(HF)_\delta$ is exposed to liquid HF and not pumped, a $c$-axis expansion of 0.5 to 0.6 Å is found, corresponding to the uptake of one
molecule of HF for every 11 - 14 carbon atoms. Electrochemical cells employing \( C_{x} F_{1-\delta}(HF)_{\delta} \) with HF/NaF as the electrolyte generally have internal resistances about 1/10 to 1/20 of those with aqueous alkali fluoride or organic (e.g., propylene carbonate/LiPF\(_{6}\)) electrolytes. Clearly, the interaction of HF with the graphite fluoride is strong. It appears to bind tenaciously to the host lattice and can assist in the removal of fluoride ions. The most likely HF binding mechanism is through hydrogen bonds to the C-F fluorines which appear, from XPS studies [Mallouk & Bartlett 1983], to bear a partial negative charge. The \(^1\)H n.m.r. spectrum of \( C_{2.15}F_{0.83}(HF)_{0.17} \) shown in figure 5, provides a measure of the strength of this interaction. The linewidth (37 ppm) is indicative of hindered rotation or diffusion of the proton-containing species at 20°C, which occurs with an activation enthalpy of about 11 - 12 kcal mole\(^{-1}\). Alternatively, the protons in \( C_{x} F_{1-\delta}(HF)_{\delta} \) could be present in ionic species such as HF\(_2^-\), which are relatively fixed in the gallery and so cannot undergo rotation or exchange at 20°C. This model appears unlikely, however, since significant concentrations of anions in the galleries, and equivalent hole concentrations in the carbon sheets, would be expected to give rise to electronic conduction in \( C_{2.0} F_{1-\delta}(HF)_{\delta} \). The observed resistivity of the latter is in excess of \( 10^7 \Omega\)-cm.
X-ray powder data [Mallouk & Bartlett 1983], together with the vibrational and $^{13}$C n.m.r. spectra, establish that the carbon atoms in $\text{C}_x \text{F}_{1-\delta} (\text{HF})_\delta$ are arranged in virtually undistorted, planar sheets, as are the carbon atoms in graphite. Raman spectra of $\text{C}_x \text{F}_{1-\delta} (\text{HF})_\delta$ suggest that the fluorine atom array is ordered in small (50 - 100 Å) domains. Twinning and haphazard stacking of such domains can account for the observed loss of diffraction intensity (table 2) for $hk\ell$ ($\ell \neq 0$) reflections with increasing Bragg angle.

There are two notable features of the X-ray powder data for $\text{C}_x \text{F}_{1-\delta} (\text{HF})_\delta$. One is the marked increase in $c_0$ spacing [Mallouk & Bartlett 1983] for $x$ values less than 3. The other is the disappearance of $hk\ell$ reflexions for $x$ values less than 3. Evidently there is close packing of the sheets for $x$ values of three or greater. That, as $x$ approaches a value of 2, only $hk0$ and $00\ell$ reflexions are observed, implies that there is little or no registry of positioning of one sheet relative to its neighbours. Because of the electrochemical reversibility of the synthesis of $\text{C}_x \text{F}_{1-\delta} (\text{HF})_\delta$ ($x \geq 2.6$), it is reasonable to assume that the F ligands can easily relocate to provide for their greatest separation, at any composition. Figure 6 shows the F ligand distributions to be expected for $\text{C}_3 \text{F}$.
and $C_2F$ stoichiometries ($F$ signifying $F$ and HF in these instances). The $C_3F$ arrangement provides for interlocking of the layers and close packing. The $C_2F$ arrangement does not. Since the van der Waals' diameter of fluorine is about $2.7 \AA$, it is likely that the occurrence of two $C - F$ linkages on the same side of the sheet in meta ring positions would be sterically unfavorable; the closest $F - F$ contacts in such an arrangement would be only $2.46 \AA$. For this reason the meta contact models are not included in figure 6.

The $C - F$ bond in $C_x F_{1-\delta} (HF)_\delta$ is clearly unusual. Electrons which are withdrawn from the graphite $\sigma$ or $\pi$-system to form these bonds must still be used in $C - C$ bonding, since the carbon-atom sheets have practically the same dimensions and stretching frequencies as in graphite itself. The bonding molecular orbital composed of fluorine $sp$ and carbon $P_z$ atomic orbitals is of appropriate symmetry to overlap with the neighboring carbon $P_z$ orbitals, and so some $\pi$-bonding will be maintained. Nevertheless, electrons in this bonding combination must be strongly localized near the fluorine atom, and thus the electronic conductivity of the sheet is diminished. The $C - C \pi$-bond order may be preserved if the carbons make, in the language of valence bond theory, one-electron dative bonds to the fluorine atoms. These electrons bestow a partial negative charge on the fluorine atoms and are at the same time used in $\pi$-bonding within the carbon network.

**Summary**

Vibrational and n.m.r. spectra, together with X-ray structural data, have established that the carbon atom sheets of $C_x F_{1-\delta} (HF)_\delta$ ($2 \leq x \leq 5$) are planar.
and nearly isodimensional with those of graphite. Fluorine atoms are found to eclipse carbon atoms in the structure, making weak, two-center C–F bonds. HF is present in the structure and binds to these fluorine atoms via hydrogen bonds.

The authors gratefully acknowledge the support of the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

References

Figure 1. Raman spectra of first stage graphite hydrofluorides.
Figure 2. Infrared spectrum of $\text{C}_2\text{.SF}_{1-\delta}(\text{HF})_{\delta}$. 
Figure 3. $^{13}$C nmr spectra of (a) $C_{3.7}F_{1-6}(HF)_{6}$ and (b) $C_{2.05}F_{1-6}(HF)_{6}$. 
Figure 4. Variable contact time $^{19}_F \rightarrow ^{13}_C$ cross-polarization nmr spectra of $C_{2.05}F_{1-\delta}(HF)_\delta$. 
Figure 5. Proton nmr spectrum of $\text{C}_{2.15}F_{0.83}(\text{HF})_{0.17}$.
Figure 6. Structural models for (a) $C_3F$ and (b) $C_2F$.

(The unshaded circles represent the fluorine atoms on one side of a carbon-atom sheet and the shaded circles represent the fluorine atoms of an adjacent sheet in positions of closest packing.)
Table 1. Observed and calculated $^{13}$C nmr intensities for $C_{2.05}F_{0.82}(HF)_{0.18}$

<table>
<thead>
<tr>
<th>Contact Time (ms)</th>
<th>Low Field Peak</th>
<th>High Field Peak</th>
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<tr>
<td></td>
<td>I(obs)</td>
<td>I(calc)</td>
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<td>20.00</td>
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<td>72</td>
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</table>

Low field carbons: $T_{CF}^1 = 0.40(5)$ ms, $N_1 = 0.78(10)$
$T_{CF}^2 = 2.49(8)$ ms, $N_2 = 0.79(10)$

High field carbons: $T_{CF} = 0.10(2)$ ms, $N = 1.00$

Fluorine $T_{1p} = 6.0(5)$ ms
Table 2. X-ray powder diffraction data for $C_{2.49}F_{1-\delta}(HF)_{\delta}$.

<table>
<thead>
<tr>
<th>int</th>
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<th>$1/d^2$(calc)</th>
<th>hkl</th>
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</tr>
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The radiation source was MoKα. $a = 2.457(3)$, $c = 6.01(5)$ Å

*hk0 intensities were calculated using $x,y = \pm(1/3, 2/3)$ for C and F.

**intensities calculated using carbon $x,y = \pm(1/3, 2/3)$ and fluorine $x,y = \pm(.365, .635)$.

No corrections were made for absorption or thermal motion.
Legends

Figure 1. Raman spectra of first stage graphite hydrofluorides.

Figure 2. Infrared spectrum of $C_{2.5}F_{1-δ}(HF)_δ$.

Figure 3. $^{13}C$ nmr spectra of (a) $C_{3.7}F_{1-δ}(HF)_δ$ and (b) $C_{2.05}F_{1-δ}(HF)_δ$.

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(The unshaded circles represent the fluorine atoms on one side of a carbon-atom sheet and the shaded circles represent the fluorine atoms of an adjacent sheet in positions of closest packing.)
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