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1115

X-ray Photoelectron and NMR Studies of Polyfluorinated C60: Evidence That C-C Bonds Are Broken

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Abstract: In order to better understand the properties and composition of solids of polyfluorinated C_{60}, X-ray photoelectron spectroscopy (XPS) was used to characterize several different $C_{60}F_x$ samples synthesized in two diferent laboratories. Quantitative measurements of the F_{1s}, C_{1s}, and O_{1s} XPS signals established the elemental stoichiometry of each sample. The F/C ratios for the different samples ranged from 28/60 to 53/60 in general agreement with previous mass spectroscopy studies of each sample. C_{1s} energies and shifts as well as solid-state nuclear magnetic resonance studies provided additional information about the degree of fluorination and level of C-C bond breaking.

Introduction

Recently, there has been considerable interest in preparing and characterizing highly fluorinated fullerenes[1-3] because of their novel structure and potential use for lubrication.[2] In order to better understand the properties and composition of solids of polyfluorinated C_{60}, we have used X-ray photoelectron spectroscopy (XPS) to characterize several different $C_{60}F_x$ samples from two different laboratories. This paper reports quantitative measurements of the F_{1s}, C_{1s}, and O_{1s} XPS signals from which the elemental stoichiometry of each sample is calculated. Careful examination of the C_{1s} energies and shifts provides additional information about the degree of fluorination and level of C-C bond breaking in the different samples. Lastly one sample was examined by solid-state, $^{19}F-^{13}C$ cross polarization/magic angle spinning ^{13}C nuclear magnetic resonance spectroscopy.

Results and Discussion

A. Quantification of C, F, and O. The integrated C_{1s}, F_{1s}, and O_{1s} XPS signals are used to determine to the elemental carbon, fluorine, and oxygen stoichiometries of each sample. Examination of the results of these measurements given in Table 1 shows that both the FBB sample from U. Tenn. and the sublimed $C_{60}F_x$ sample from U. Penn. appear to be quite similar in elemental

Table 1. Summary of the Carbon, Fluorine, and Oxygen Stoichiometries for Polyfluorinated C_{60} Samples Relative to Those of C_{60}

sample	elemental composition[b]					sample origin
	C	F	O	F/C	F/O	
FBB[a]	60	38	3.4	0.58	10.3	U. Tenn.
HFBB[a]	60	53	2.6	0.80	18.5	U. Tenn.
starting $C_{60}F_x$	60	28	6.0	0.43	4.3	U. Penn.
sublimed $C_{60}F_x$	60	37	3.0	0.59	11.8	U. Penn.
residual C_xF_x	60	35	4.7	0.54	6.9	U. Penn.
C_{60}	60		1.5			this work

[a] FBB is fluorinated buckyball (C_{60}), and HFBB is hyperfluorinated buckyball (C_{60}). [b] The experimental sensitivity factors for our XPS system as supplied from the manufacturer[4] are 1, 0.71, and 0.296 for F_{1s}, O_{1s}, and C_{1s}, respectively. In order to confirm that our system was actually performing as advertised, we independently determined the sensitivity factors for fluorine and carbon using Teflon as a reference material with a known F/C ratio of 2.0. Using the manufacturer's original sensitivity factors, an F to C ratio of 2.7 was obtained for Teflon. As a result we correct all data to reflect a higher F sensitivity relative to C. We assume for the present that the C to O sensitivity is unchanged, but we will be running reference materials with known C to O compositions in the near future. For the present purposes, quantification of oxygen is not critical to the main conclusions of this paper.

composition, $\approx C_{60}F_{37}O_3$, and in reasonable agreement with expectations from mass spectrometric investigations[3,5] of similar samples.[6] The HFBB shows the highest fluorine content with the F/C ratio increasing from 0.63 (38:60) for the FBB sample, fluorinated C_{60}, to 0.88 (53:60) for the HFBB sample, hyperfluorinated C_{60}.

As seen from Table 1 and consistent with earlier mass spectrometry characterizations,[3,5] evidence for oxygen is also observed in all samples. In comparing the three U. Penn. samples we note the following: The sublimed $C_{60}F_x$ sample not only shows a significant increase in the fluorine to carbon ratio (from 0.47 to 0.62) compared to that of the starting material but also exhibits the highest F/O (or C/O) ratio. The residual fraction exhibits F/C and F/O values intermediate between the starting material

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(6) Mass spectrometry suggests the most abundant peak for the FBB sample is $C_{60}F_{46}$[3] whereas for the sublimed $C_{60}F_x$ sample, $C_{60}F_{40}$ is the most abundant peak.[5] These observations lend support to the suggestion that gas-phase stoichiometry may not accurately reflect the bulk stoichiometry.

1116 *J. Am. Chem. Soc., Vol. 116, No. 3, 1994*

Cox et al.

Table 2. Experimental C_{1s} Binding Energies and Shifts (eV) for Fluorinated Polyethylene, Small Fluorinated Molecules, and an F-Intercalated Graphite Sample[a]

	C_{1s} binding energy	shift, ΔC_{1s}	C_{1s} binding energy	shift, ΔC_{1s}
$-CH_2-CH_2-$	285.0[b]	0.0	284.6[c]	0.0
$-CHF-CH_2-$	285.9[b]	0.9	285.5[c]	0.9
$-CHF-CH_2-$	288.0[b]	3.0	287.7[c]	3.1
$-CHF-CHF-$	288.4[b]	3.4		
$-CH_2-CF_2-$	286.3[b]	1.3	286.4[c]	1.8
$-CH_2-CF_2-$	290.8[b]	5.8	290.9[c]	6.3
$-CHF-CF_2-$	289.3[b]	4.3	289.4[c]	4.8
$-CHF-CF_2-$	291.6[b]	6.6	291.6[c]	7.0
$-CF_2-CF_2-$	292.2[b]	7.2	292.2[c]	7.6
F-intercalated graphite, CF_x	285[d]	0.0		
	289.9[d]	4.9		
HCF_3	294.7[e]	9.7[e]		
CF_4	296.7[e]	11.7[e]		

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and the sublimed fraction. Possible explanations for this behavior are likely some combination of effects such as (a) the fluorided oxides are less thermally stable than "pure" fluorides of C_{60}, thus accounting for decreased O and increased F content in the sublimed sample, or (b) certain stoichiometries of highly fluorided C_{60} may more readily sublime than some of the less highly fluorided C_{60}, suggesting lower heats of desorption with increasing levels of fluorination. The resulting stoichiometry thus may be a sensitive function of the thermal history of the sample prior to or during any measurement.

Since all samples are observed to have some oxide contamination, it now becomes critical to our understanding of the true chemical nature of these materials to be able to obtain "pure" materials. Not only must the fluorine oxide material be separated from the clean fluorinated material but the separation of the C_{60} fluorides must be accomplished. The recent report that the oxygen in $C_{60}F_xO_y$ species is bound as an epoxide and not as fluoroxy species[7] is a good first step in the direction. In addition, the F_{1s} XPS signals show no evidence of structure. This is consistent with the expectation that the F atom is in a single chemical environment, i.e. F is bonded only to C and any fluoroxy species, if they are present, are present in such low abundance as to be undetectable. These observations confirm speculations from earlier mass spectrometry experiments[3,5] but more importantly reveal a possible chemical route to remove epoxides from polyfluorinated C_{60}.

B. Interpretation of C_{1s} Core Level Shifts. It is well established both experimentally[8-10] and theoretically[11] that the C_{1s} core level energy exhibits substantial shifts due in large part to the strong electron-withdrawing character of fluorine. This is illustrated in Table 2 where the XPS energies and shifts of different fluorinated polyethylenes, other fluorinated molecules, and a fluorine intercalated graphite compound are tabulated. For carbons bonded only to other carbons and/or to hydrogen, the C_{1s} core level energy remains near 285 eV, as observed for pure C_{60}[12] or polyethylene.[10] In polyethylenes, substitution of fluorine for hydrogen on the primary carbons results in shifts ranging from 2.5 to 3.2 eV per F substitution, with an average shift of $\approx$2.9 eV.[10] Substitution

of fluorine for hydrogen on nearest neighbor carbons causes a secondary shift which varies from 0.4 to 0.9 eV with an average shift of $\approx$0.7 eV.[10]

The energy shifts due to substitution effects on fluorinated materials are useful guides in interpreting the XPS results for polyfluorinated C_{60}. Specifically for carbons which exhibit no shift, one can be confident that no F is bonded to the primary carbon atom and, equally important, no fluorine is bonded to any of the three nearest neighbor carbons; otherwise a primary shift of $\approx$2.9 $\pm$ 0.3 eV and/or a secondary shift of $\approx$0.7 $\pm$ 0.3 eV per attached F could be anticipated. Thus primary carbon shifts varying from a minimum of $\approx$2.9 $\pm$ 0.3 eV up to a maximum of 5.0 $\pm$ 1.2 eV might be expected for polyfluorinated C_{60}, assuming no more than one F atom bonds to a given carbon atom in C_{60}, i.e. the carbon shell remains intact. Secondary shifts varying from a minimum of 0.7 $\pm$ 0.3 eV to a maximum of 2.1 $\pm$ 0.9 eV would be predicted for C atoms which have no F directly bonded to them but have some nearest neighbor carbons with fluorine bonded to them. For carbons which have two or more F's bonded to them, a shift of $\geq$5.8 $\pm$ 0.6 eV would be predicted but, even more significantly, some carbon–carbon bonds in C_{60} must have broken to accommodate formation of CF_2 (or CF_3) moieties. Formation of CF_3 moieties would manifest itself as C_{1s} XPS shifts on the order of 9 eV or greater. As will be seen below, two of the C_{60} samples, those with the highest levels of fluorination, do show evidence for C–C bond breaking.

What do the C_{1s} XPS studies show? Figures 1–3 present typical spectra from our studies. Figure 1 compares XPS spectra from four different samples, two reference materials (Teflon, poly-(tetrafluoroethylene) (PTFE) with $(-CF_2-CF_2-)_x$ monomeric building blocks, and a fluorine-intercalated graphite sample CF_x) and two fluorinated C_{60} samples labeled FBB and HFBB.[3] Table 3 presents the peak energies and areas from spectral deconvolution of the spectra shown in Figures 1, 2, and 3. The spectrometer energy scale was initially calibrated with respect to copper. Since the fluorinated samples were not highly conducting, each spectrum was referenced to the F_{1s} peak (688.75 eV for Teflon) to correct for charging effects. This procedure does introduce some uncretainty ($\pm$0.5 eV) in the absolute energies since the F_{1s} energy has been reported to vary slightly dependent upon the level of fluorination of fluorocarbons.[10] Nevertheless this uncertainty is relatively small compared to the shift of C_{1s} upon fluorination.

As is readily observed in Figure 1, Teflon has only a single C_{1s} peak centered near 292.2 eV, a shift of about 7.2 eV. This is consistent with a homogeneous sample consisting only of F_2C–CF_2 groups. For the F-intercalated graphite sample two main peaks are observed, the stronger one containing about 81% of the C_{1s} signal occurs at 289.9 eV and a weaker one at 285 eV. The C/F ratio for this sample is about 1, suggesting that on average each carbon is bonded to one fluorine atom.

By following the road map as given in Table 2, the peaks are assigned as shown in Table 3. For example, the 7.2-eV peak for PTFE is accounted for as the sum of a primary shift $\approx$5.8 eV due to two fluorines bonded to this carbon atom plus a secondary shift ($\approx$1.4 eV) due to fluroine bonded to the two nearest neighbor carbons. For the F-intercalated graphite sample, the 285-eV peak is assigned to a bare carbon and the 289.9-eV peak is accounted for as the sum of a primary shift $\approx$2.9 eV plus a secondary shift of 3 $\times$ 0.7 = 2.1 eV due to a fluorine on each of the three nearest neighbor carbons. In addition, a weak shoulder observed on the high energy side of the 289.0-eV peak suggests some CF_2 bonding which could be due to additional fluorines bonding to edge carbons located at the periphery of individual

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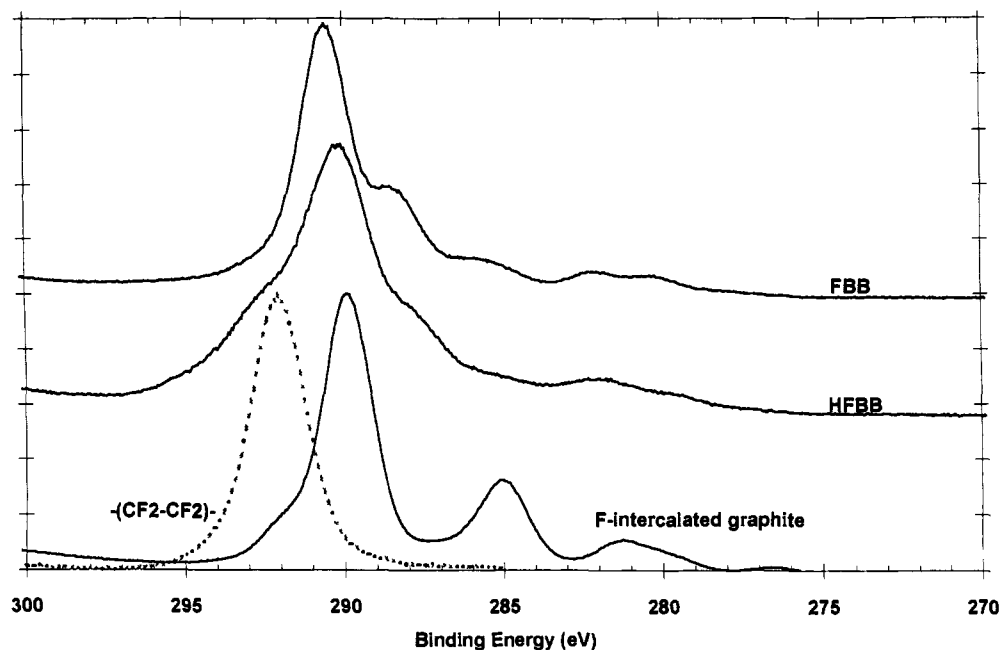
Figure 1. Comparison of C_{1s} XPS spectra for two fluorinated reference materials, teflon and F-intercalated graphite, and two polyfluorinated C_{60} samples, FBB and HFBB. All XPS spectra were obtained using non-monochromatic Mg K_α X-rays at 1253.6 eV. The weak peaks observed below 285 eV are due to emission from satellite X-ray lines.
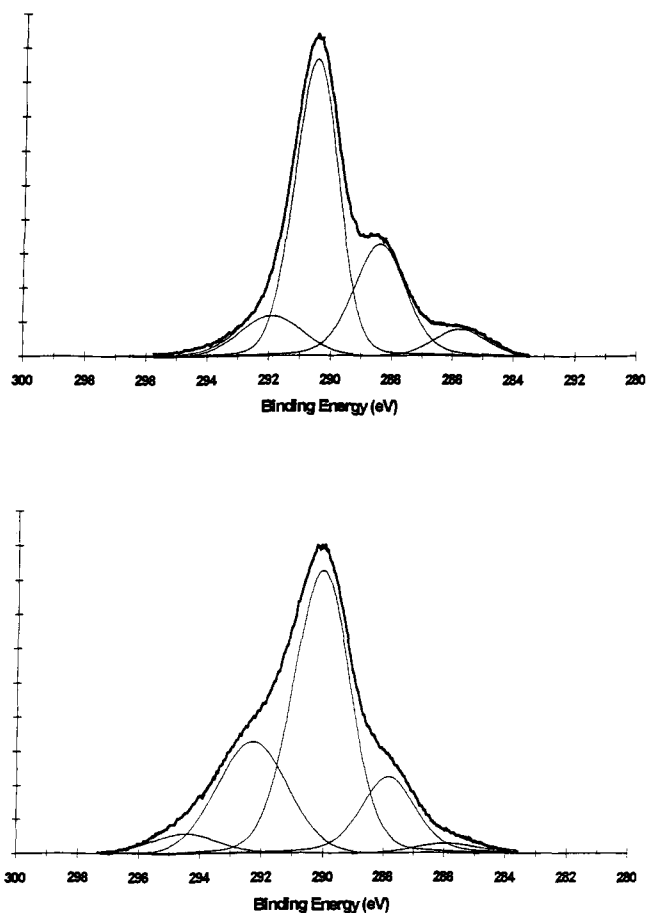

Figure 2. Peak analysis from spectral deconvolution of the C_{1s} X-ray photoelectron spectrum of the FBB (upper plot) and HFBB (lower plot) samples. The peak energies and peak areas for the samples together with results from similar analysis of the other samples are given in Table 3.

graphite layers. The 285-eV peak suggests either some fraction ($\approx 19\%$) of the graphite did not get fluorinated or possibly some hydrocarbon contamination.

The XPS spectra from two different fluorinated C_{60} samples synthesized at the University of Tenessee are also shown in Figure

1. The sample labeled FBB is fluorinated buckyball and was prepared identically to other samples from the same group which previously have been subjected to mass spectrometry[3] and UV photoemission[13] characterization. The mass spectrometry showed that $C_{60}F_{46}$ was the most abundant species, but significant signals were observed for $C_{60}F_x$ for $x < 46$. Using UV photoemission, Benning et al.[13] reported measurements of the C_{1s} region from a film prepared in situ by subliming a polyfluorinated C_{60} sample prepared similarly to the FBB sample. They observed two peaks for this sample, one at 285 eV and one at 287.3 eV. The present C_{1s} XPS measurements (Figure 1) on what is believed to be a nearly identical sample of FBB show a nearly identical spectrum except that the two main peaks are found to be centered around somewhat higher energies of 288.4 and 290.5 eV. The possible reasons for this difference will be discussed below.

For the FBB sample shown in Figure 1, the largest XPS signal is observed near 290.5 eV, a 5.5-eV shift. This peak is thus assigned as $C-F$ with some, possibly all, nearest neighbor carbons also having fluorine bonded to them. Note that, if none of the three nearest neighbor carbons had F attached, an energy shift if only 2.9 ± 0.3 eV would be expected. Thus the shoulder on the low-energy side of the 5.5-eV main peak is likely indicative of a primary $C-F$ carbon, some of whose nearest neighbor carbons do not have F attached, i.e. an effective broadening and shifting of the primary peak by one, two, and three nearest neighbor secondary shifts. In addition, some intensity is observed near 286 eV, a 1-ev shift, together with broadening of this peak toward higher energy. Such effects are indicative of carbon atoms with no attached fluorine but some of whose nearest neighbor carbons do have attached F. From the deconvolution of the FBB XPS spectrum, Figure 2 (top), there is evidence for some C_{1s} signal ($\approx 9\%$) shifted about 6.9 eV, suggestive of some $C-F_2$ formation, i.e. some $C-C$ bond breaking in some of the $C_{60}F_x$ molecules in this sample.

The sample in Figure 1 labeled HFBB, hyperfluorinated C_{60}, is a second sample synthesized at U. Tenn. This sample was prepared by refluorinating FBB while irradiating with light as described elsewhere.[14] Comparison of the C_{1s} XPS spectra

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Table 3. Experimental C_{1s} XPS Energy Shifts (eV) and Percent Areas (in parentheses) Obtained from Spectral Deconvolution of the Spectra[a]

	samples						
	reference materials		from U. Tenn.		from U. Penn.		
	PTFE	CF$_x$	FBB	HFBB	sublimed	residue	raw
C w/o F		0.0 (19)			0.3 (2)		0.0 (17)
NN w/o F		±0.8			±1.0		±1.0
$\Delta C_{1s} \approx 0$ eV							
C w/o F[b]			0.8 (6)	0.9 (2)	1.7 (13)	1.3 (14)	2.1 (32)
some NN w F			±1.0	±1.2	±1.5	±1.2	±1.1
$\Delta C_{1s} \approx 0.7$–2.1 eV							
C w F			3.4 (27)	2.8 (15)	3.3 (31)	3.4 (32)	
few NN w F			±1.0	±1.0	±1.0	±1.2	
$\Delta C_{1s} \approx 2.9$–5.0 eV							
C w F		4.9 (72)	5.5 (58)	5.1 (54)	5.5 (54)	5.7 (54)	5.0 (51)
some NN w F		±0.9	±0.8	±1.1	±1.1	±1.2	±1.0
$\Delta C_{1s} \approx 2.9$–5.0 eV							
C w F$_2$	7.2 (100)	6.8 (9)	6.9 (9)	7.3 (25)			
some NN w F, F$_2$	±1.0	±0.9	±1.2	±1.4			
$\Delta C_{1s} \approx 5.0$–7.2 eV							
C w F$_3$				9.5 (4)			
$\Delta C_{1s} \approx 8.7$–10 eV				±1.3			

[a] Possible assignments are given in the left-hand column. All energy shifts in the table are referenced to 285 eV for bare carbon. The energy scale itself is referenced to F_{1s}.[18] The ± values in the table reflect $^1/_2$ the FWHM of the peaks obtained from deconvolution of the XPS spectra. The terminology for the first column: C w/o F means carbon without any attached fluorine, NN w F means some first nearest neighbor carbons to the one being measured have (with) some attached fluorine(s), etc. The ΔC_{1s} values in column 1 are the approximate ranges of XPS shifts which might be expected upon the basis of studies of poly(fluoroethylenes). [b] This shift is tentatively assigned to the primary carbon with no fluorine, but some of whose nearest neighbor carbons do have a fluorine bonded to them. Since some oxygen is observed in these samples, it is possible that some of this signal could be due to oxidized $C_{60}F_x$, since oxide can lead to a C_{1s} shift on the order of 1.5 eV.[20]

between FBB and HFBB shows a growth of intensity toward higher binding energy for the HFBB and a concomitant decrease in the intensity at lower binding energy, effects consistent with higher fluorination levels. The high-energy shoulder near the 6.5–7-eV shift, characteristic of CF$_2$ type carbons, comprises a significant fraction ($\approx$25%) of the total C_{1s} signal (Table 3) and is taken as direct proof that some carbon atoms have more than one fluorine attached and thus the C_{60} carbon shell has at least partially opened up. This is consistent with recent mass spectrometry studies[14] for a similar sample of polyfluorinated C_{60} which not only shows evidence for perfluorinated C_{60}, $C_{60}F_{60}$, but also reports mass peaks assigned to $C_{60}F_x$ where $x > 60$, i.e. hyperfluorinated C_{60}. From the deconvolution of the C_{1s} spectra shown in Figure 2 (bottom), there is evidence for some C_{1s} signal ($\approx$4%) shifted about 9.5 eV, suggestive of a small amount of –CF$_3$ formation as well.

XPS studies of three polyfluorinated C_{60} samples synthesized at U. Penn. have also been carried out. Details on the preparation and other characterizations of these samples are discussed elsewhere.[15] These three samples are labeled as (a) starting material, (b) sublimed fraction, and (c) residual fraction. The XPS spectra of these three samples are compared in Figure 3, and the results from the spectral deconvolution are summarized in Table 3. The starting material is polyfluorinated C_{60} as initially prepared, the sublimed fraction is polyfluorinated C_{60} which has been separated from the starting mateiral by sublimation, and the residual fraction is the polyflorinated C_{60} material left behind after sublimation of the starting material.

Qualitatively, the XPS spectra are similar to those from the FBB and HFBB samples. All three samples show a strong peak comprising over 50% of the total C_{1s} signal and shifted between 5 and 5.7 eV. This main peak near 290-290.7 eV (shift of 5–5.7 eV) again is assigned as C–F type carbons with mostly C–F nearest neighbor carbons. For the sublimed and residual fractions, the shoulder on the low-energy side of this main peak (shift of 3.3– 3.4 eV) is assigned to C–F carbons with some bare C atoms as nearest neighbors. The remaining C_{1s} signal ($\approx$15% of the total C_{1s} signal) is assigned to bare carbons which have some nearest

neighbor carbons with attached F. For the starting material, the lower energy peaks comprise about 49% of the total C_{1s} signal and suggest a larger fraction of the carbons have no fluorine bonded to them. Note from Table 3 that the spectral deconvolution of the starting material spectrum shows evidence for some C_{1s} intensity (17% of the C_{1s} signal) at 285 eV, which could be bare C_{60}. Since the sublimation temperature was only 300 °C and bare C_{60} does not readily sublime at that temperature, nonfluorinated C_{60} presumably would be left behind during the sublimation process.[16] No evidence for CF$_2$ or CF$_3$ formation (hyperfluorination) is observed in the U. Penn. samples.

C. Discussion of Prior C_{1s} Results. Nakajima and Matsuo[17] have also recently reported XPS of several samples of fluorinated C_{60} with nominal composition $C_{60}F_{40}$ which were prepared in their laboratory. Although the spectra were not published, the description suggests that the general shape of the C_{1s} spectrum would be similar to that of FBB or the sublimed sample in this work, except for a possible energy scale shift. They report three C_{1s} peaks shifted by –0.4, 1.5, and 3.4 eV relative to bare C_{60}. From our studies, we would suggest that the first peak is due to bare carbon and the middle peak to bare carbons, some of whose nearest neighbor carbons (about two out of three) have fluorine bonded to them. Similarly the 3.4-eV shifted peak can be attributed to the primary carbon with fluorine plus fluorine also on some nearest neighbor carbons. Again absolute energies are somewhat uncertain due to difficulties in referencing nonconducting substrates and likely account for much the difference in peak energies observed in the two measurements. They report no evidence of larger shifts indicative of multiple fluorines on individual carbons and thus C–C bond breaking in C_{60}.

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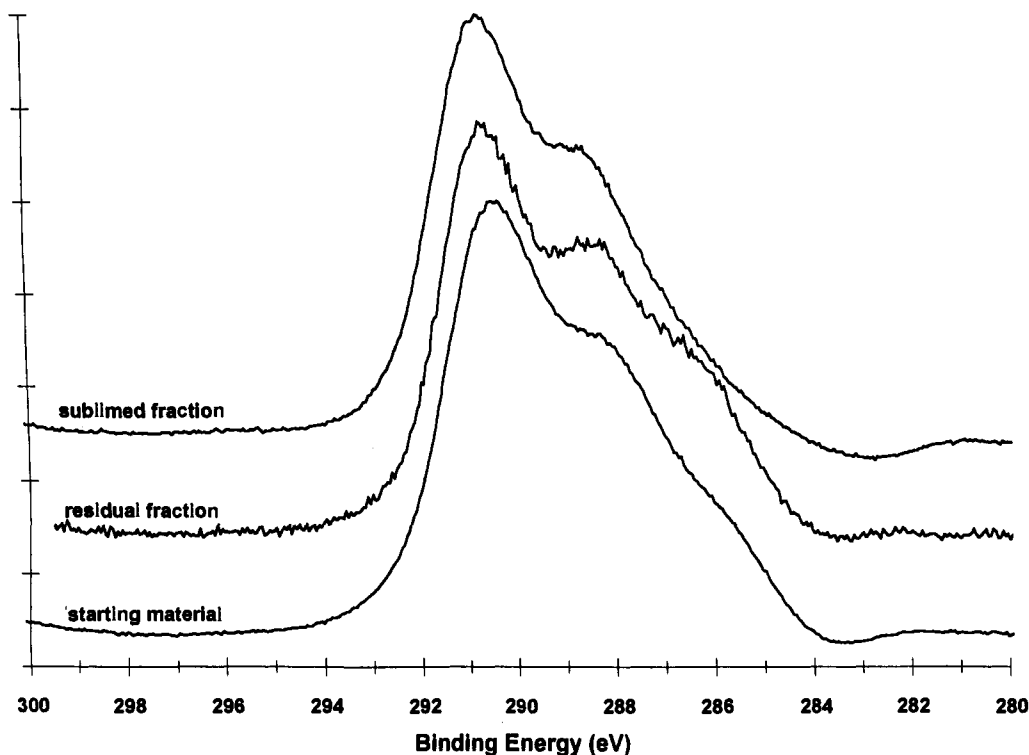
(16) It is not unreasonable to expect that sublimation properties of $C_{60}F_xO_y$ materials will be dependent on the level of fluorination (x) and/or oxidation (y). Results from these and other similar samples suggest that up to a point the more highly fluorinated materials sublime more readily than their less highly fluorinated cousins. In addition, the thermal stability of $C_{60}F_x$ ($C_{60}F_xO_y$) materials may be sensitive to the level of fluorination. At the highest levels of fluorination, e.g. for fluorination levels above 48, mass spectroscopy studies show a pronounced drop in signal intensity, an effect which could be due to a significant decrease in thermal stability for C_{60} with more than 48 fluorines. On the other hand, the evidence for CF$_2$ groups suggests that the carbon shell may begin to open up at these high levels of fluorination. An opened C_{60} would likely have significantly different desorption and thermal stability properties.

(17) Nakajima, T.; Matsuo, Y. *Carbon* 1992, *30*, 1119.

Figure 3. XPS spectrum of three samples of polyfluorinated C_{60}: the starting material prior to sublimation, a sublimed fraction, and the residual fraction remaining after sublimation. See Table 3 for numerical values from the spectral deconvolution.

Benning et al.[13] reported UV photoemission measurements of C_{1s} core level emission from a film believed to be polyfluorinated C_{60} with composition $C_{60}F_{46\pm2}$. This film was prepared by in-situ sublimation of polyfluorinated C_{60}. Two peaks were observed, one centered at 284.9 eV and the other at 287.2 eV with relative intensities of 4:1. Since a photon energy of 380 eV was used in those measurements, emission from the F_{1s} and O_{1s} core levels could not be measured and independent measurement of the F:C:O ratio could not be obtained.

As can be seen from Figure 1, the XPS spectrum for FBB (supposedly a sample nearly identical to that which Benning et al. used) shows a shape similar to that obtained in UV photoemission studies of Benning but exhibits substantially higher energy shifts. Benning et al. assigned their low-energy peak (285 eV) to C atoms with no fluorine attached and the higher energy peak to C atoms with F attached. However, as discussed above, no C_{1s} shift implies that not only does the primary carbon have no F attached but its three nearest neighbor carbons also must have no F attached. Similarly, the peak 2.3 eV higher suggests that F could be attached to the C, but this shift is not sufficiently large to expect nearest neighbor carbons to also have F attached. Thus, if their energy scale is correct, the average stoichiometry of fluorinated C_{60} in the UV photoemission studies is predicted to be about $C_{60}F_{12}$.[18] One possibility lies with the difficulties in establishing an energy scale in nonconducting samples.[19] Shifting the peaks observed at 284.9 and 287.2 eV about 1–3 eV to higher binding energy would bright their results into reasonable agreement with the expected properties of the nonsublimed sample, i.e. stoichiometry consistent with $C_{60}F_{46}$ and C_{1s} core level energies consistent with that expected for C–F groups on highly fluorinated C_{60}. A second possibility is that the sublimation temperature (not given in ref 13) was sufficiently high that (i) any bare C_{60} would sublime directly or (ii) some $C_{60}F_{46\pm2}$ underwent defluorination producing $C_{60}F_x$ ($x \ll 46$), which subsequently

sublimed. In this manner a film containign a combinationof bare C_{60} and/or partially defluorinated $C_{60}F_x$ ($x \ll 46$) might be produced.

D. Solid-State NMR. A sample of $C_{60}F_{46}$ prepared by the University of Tennessee group in the same manner as the FBB sample discussed earlier was examined by solid-state, ^{19}F–^{13}C cross polarization/magic angle spinning (CP/MAS) ^{13}C spectroscopy.[21] A study of this material as a function of the ^{13}C–^{19}F cross polarization contact time provides incontrovertible evidence that the sample is a mixture of materials that are spectroscopically distingishable based on molecular motion characteristics. The component with rapid molecular reorientation, similar to that observed for spherical plastic crystal, displays an sp^2:sp^3 resonance area ratio of approximately 14:46 corresponding to the stiochiometry found by mass spectrometry. These sp^2 carbon resonances, 140.0–142.5 ppm, have chemical shift and cross polarization dynamics which indicate the absence of directly bonded fluorine. The same criteria dictate that the 86–90-ppm sp^3 carbon resonances arise from fluoromethine sites. This spectral data is that anticipated for $C_{60}F_{46}$. A second component in the spectrum is observable as a broad resonance (half-height line width of ca. 40 ppm) centered at 118 ppm, the chemical shift region of geminal

(18) Twenty percent of the intensity assigned to C with no F attached → 12 carbons plus the three nearest neighbors of these 12 carbons = 48 carbons with no F attached. Alternatively, 80% with one F attached and three without F attached → 48 carbons affected, of which 12 have F and 36 do not have F attached.

(19) The energy scale was determined using the following procedure. Due to charging effects (5–10 eV) on these nonconducting samples, powders pressed onto one side of double-sided tape mounted on the XPS metal stub, calibration of the energy scale was a serious concern. In a non-monochromatic XPS source such as used here, the positive charging of the sample is nearly neutralized by the low-energy electrons emitted from the x-ray window, resulting in a typical charging of only 5–10 eV.[20] Since all samples contained fluorine and the F_{1s} energy remains relatively constant for different levels of fluorination (±0.5 eV), we chose to reference each sample's energy to that of the F_{1s} line at 688.75 eV. The value of 688.75 eV was obtained from a Teflon sample that contained adventitious carbon whose C_{1s} energy is 285 eV. The individual spectra were then corrected for charging effects by shifting the energy scale to give 688.75 eV as the F_{1s} energy. This leads to some uncertainty in the energies since the F_{1s} energy does have a weak dependence (±0.5 eV) on the level of fluorination. The energy scale under noncharging conditions was calibrated in separate experiments.

(20) Beamson, G.; Briggs, D. *High Resolution XPS of Organic Polymers*; John Wiley & Sons: New York, 1992; p 26.

(21) The NMR spectra were recorded on a Bruker msl 100 spectrometer operating at 2.35 T. Magic angle spinning (4.2 kHz) and ^{19}F dipolar decoupling (55 kHz) were used for all measurements.

difluorocarbon resonances. The cross polarization dynamics of this resonance are similar to those observed for molecules with slow or no motion in the solid state. This resonance contributes $20 \pm 10\%$ of the total resonance area in the spectrum. The two components described above are likely the soluble "$C_{60}F_{46}$", which is the basis for the earlier mass spectrometry results,[3] and another component (apparently insoluble since it does not appear in solution-state NMR[22] or in the mass spectrum) which contains the CF_2 groups and comprises 10–30% of the solid. These results are consistent with the XPS of FBB where about 9% of the C_{1s} signal can be attributed to CF_2 groups (see Table 3).

Summary

XPS studies of solids of $C_{60}F_x$ have allowed elemental stoichiometries to be obtained. These experiments suggest that the carbon to fluorine stoichiometry inferred from mass spectrometry experiments does not accurately reflect the F:C:O stoichiometry of the solid material. Not only does one infer a higher F:C stoichiometry from the mass spectrometry experiments but the level of oxygen appears to be somewhat lower also. Since mass spectrometry experiments can only probe volatile gas-phase species, while XPS probes the solid-phase material, such differences in fluorine and/or oxygen stoichiometries likely reflect some combination of volatility, solubility, and thermal stability of polyfluorinated C_{60}. The C_{1s} XPS studies and solid-state NMR measurements show evidence that the C–C bonds in the C_{60} shell do break and that the level of C–C bond breaking (formation of CF_2 and CF_3 groups) increases significantly as the degree of fluorination increases. The role of oxygen in all of these processes is yet to be determined. These results suggest that preparation of "pure" $C_{60}F_x$ and $C_{60}F_xO_y$ materials will be required before issues such as oxidative and thermal stabilities can be resolved.

(22) Tuinmank, A. A., et al. Private communication.