Fluorinated Fullerenes: Synthesis, Structure, and Properties

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Abstract: Solid C_{60} reacts with low-pressure fluorine at 300 K, yielding yellow-to-white solids which are air-stable for long periods, with average compositions in the range $C_{60}F_{35-44}$. Mass spectrometry reveals broad distributions of F/C ratios, with only trace amounts of perfluorofullerene $C_{60}F_{60}$. Infrared and other data indicate the presence of C–F bonds, from which we deduce a "fuzzyball" structure with fluorines externally attached to the fullerene skeleton. Most of the material sublimes in vacuum at 300 °C; molecules with F/C ratios > 48 probably decompose. The sublimed product is highly crystalline; X-ray analysis yields an average C–F bond length 1.49 Å. Thin films may be prepared by sublimation or spin-coating from solution. Contact angle measurements using water droplets suggest potentially interesting lubricating properties.

I. Introduction

Fluorocarbon chemistry has yielded a diversity of useful products, including refrigerants, Teflon, the graphite fluoride/Li battery,[1] and synthetic metals in the form of fluorine-intercalated graphite.[2] It is therefore not surprising that fluorination was among the first reactions attempted with buckminsterfullerene, the new allotrope of carbon produced in large quantities for the first time in 1990.[3] Selig and co-workers were the first to carry out reactions between F_2 gas and solid C_{60} and C_{70}.[4] Mass spectrometry, weight uptake, and infrared spectroscopy indicated broad distributions of "fluorofullerenes" C_MF_n with F atoms covalently attached to n of the available carbons, the most probable n being 36 for C_{60} and 40 for C_{70}. Subsequently, Holloway *et al.* proposed the complete fluorination to $C_{60}F_{60}$, based on the observation of a single sharp line in ^{19}F NMR.[5] Taylor *et al.* reported facile nucleophilic substitutions[6] which led them to give a pessimistic view of the potential usefulness of fluorofullerenes in an unprotected environment.[7] Tuinman *et al.* have recently carried out extensive mass spectrometric characterization of fluorofullerenes.[8] Additional data on these compounds are rapidly becoming available.[9,10]

The present paper, an extension of our earlier communication,[4] describes the synthesis, characterization, and properties of fluorinated solid C_{60}. Attempts to isolate specific compounds by chromatographic methods were unsuccessful, although sublimation of the crude product does reduce the distribution of n values somewhat. In contrast to Holloway *et al.*, we find that the perfluorinated molecule $C_{60}F_{60}$ is present in only trace amounts. Additional information about the molecular structure is obtained from X-ray diffraction. We find that $C_{60}F_n$ is quite reactive with nucleophiles *in solution* (e.g., H_2O, etc.), in agreement with earlier work.[6,7] On the other hand, $C_{60}F_n$ *solids* do not react with water and in fact survive extended exposure to air. Contact angle measurements on $C_{60}F_n$ films suggest potentially useful properties as lubricating coatings.

II. Synthesis and Characterization

Fluorinations were carried out using >99% pure C_{60} and fluorine (the latter from Spectra Gases). Our first experiments[4] were performed *in situ*, using a magnetic suspension balance (Sartorius Model 4201) to follow the weight uptake while the sample was suspended in a fluorine atmosphere. Fluorine pressure changes were measured with an MKS Baratron to ±0.1 Torr, and corresponding buoyancy corrections were applied to the weight readings. The reaction rate could thus be monitored, and the exposure was terminated when the rate of weight uptake became insignificant. Reactions proceeded rapidly during the first 10–20 min, depending on sample size, followed by a much slower approach to saturation. Figure 1 shows typical weight uptake vs time data on scales of minutes and days, although saturation was not achieved until 2–4 weeks. From a number of runs, we found saturation weight uptakes corresponding to average n values from 35 to 44, although mass peaks up to $C_{60}F_{52}$ were detected in mass spectra. Several samples were analyzed chemically for fluorine content by igniting weighed portions in oxygen in a Schöniger flask.[11] These results agreed approximately with the saturation weight uptakes, although usually showing somewhat lower fluorine content, a problem often encountered when analyzing highly

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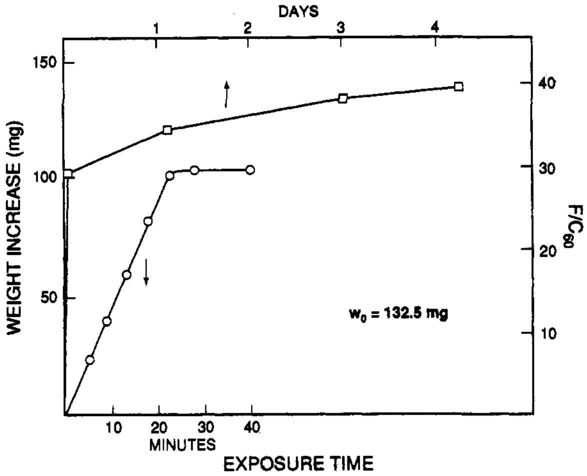

Figure 1. Weight uptake versus time for a 132.5-mg sample of extract (*ca.* 90% C_{60}, 10% C_{70}, and higher fullerenes), exposed to 200 Torr of F_2 at 300 K in a Sartorius balance.

fluorinated compounds. We found little variation in reaction rate with temperature in the range 25–70 °C. Heating to 250 °C appears to yield highly fluorinated products in a few days.[8]

In subsequent work, preparations at ambient temperature and low F_2 pressure were carried out on a monel vacuum line fitted with 3/4" diameter Kel-F sample cups, closed on one end with stainless steel Swagelok plugs and connected to the line at the other end with stainless steel Swagelok reducers and monel bellows-sealed valves. This method allows the reaction to be observed visually. Occasionally, reactions on mixtures of C_{60} and C_{70} were accompanied by flame formation, probably due to the presence of residual solvent. Flames were not observed when pure, sublimed C_{60} was used. Sometimes a stainless steel reactor was used to investigate high-pressure (3–10 atm) reactions. For large-scale preparations (>50 mg), reactions were interrupted from time to time and the product was stirred to expose fresh surfaces to the F_2 gas. In general, the crude fluorinated products were pale yellow to white in color; however in several experiments we obtained powders containing mixtures of several products varying in color from brown to white. We found no obvious correlation between color and reaction conditions.

Gaseous products from high-pressure reactions were collected by condensing into a container closed with a valve and analyzed by electron impact mass spectrometry. The main peak in the spectrum was due to $CF_3^{\bullet+}$; however, other fragments such as $C_2F_5^{\bullet+}$, $C_3F_7^{\bullet+}$, $C_4F_9^{\bullet+}$, and $C_5F_9^{\bullet+}$ were also present.

III. Optical and Mass Spectrometry

Infrared spectra of fluorinated fullerenes pelletized in KBr show a strong broad absorption at 1165 cm^{-1} characteristic of a C–F stretching vibration with partial ionic character. The C–F absorption in covalent graphite fluoride occurs at 1215 cm^{-1}.[12] This peak shifts to lower frequency with increasing fluorine uptake and has been observed as low as 1130 cm^{-1}. None of our preparations yielded peak positions as low as 1060 and 1035 cm^{-1} as reported by Holloway *et al.*[5]

Absorption spectra of pure and fluorinated C_{60} in cyclohexane are shown in Figure 2. The former is identical to that reported in the literature,[13] and the latter is in agreement with ref 8. The spectrum of the fluorinated material is typical for an electron-depleted π system. It shows a single broad absorption peak at 220 nm (5.64 eV) with a hint of a second transition at 280 nm, both falling in the range of high strength (9, 6)T_{1u} – A_g allowed transitions exhibited by pure C_{60}.[20] There are no apparent absorption peaks in the low UV and visible range for $C_{60}F_x$ dissolved in cyclohexane, dichloromethane, acetonitrile, or *n*-hexane, whereas pure C_{60} solutions reveal intense allowed $1T_{1u}$ – A_g transitions as well as a plethora of orbitally forbidden (vibrationally-assisted) transitions.[20] From the inverse photoemission data by Benning *et al.*[10] and calculations by Dunlap *et al.*[21] it follows that $C_{60}F_x$ is a wide gap insulator. The calculated HOMO–LUMO gap is 3.57 eV, although this value must be treated with caution since it was obtained assuming the full I_h symmetry for $C_{60}F_{60}$.[21] The single intense and broad absorption band could then be attributed to a transition from the molecular ground state, resulting from the overlap of the C_{60} π and F p orbitals. Further theoretical studies assuming lower symmetries would be useful to fully interpret this spectrum.

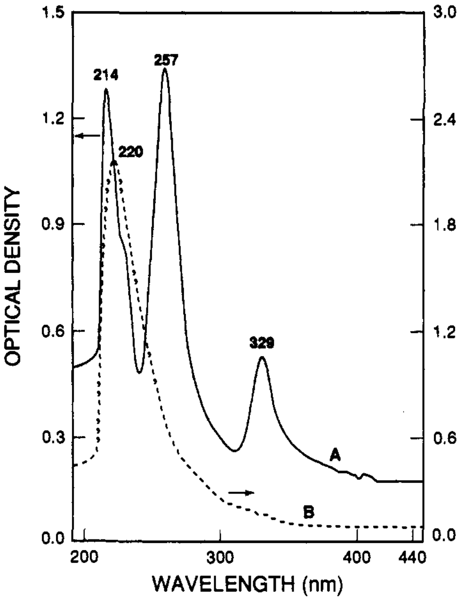

Figure 2. UV absorption spectra in cyclohexane solution: (a) pure C_{60} and (b) fluorinated C_{60}.

Mass spectra of fluorinated C_{60}-rich and C_{70}-rich samples have been published previously.[4] These show that the former contain a series of compounds with general formula $C_{60}F_{2x}$ where $15 \leq x \leq 22$ for probe temperatures of 200 °C. The most prominent peak occurs at 1404 D, indicating a particularly stable molecule $C_{60}F_{36}$, analogous to the Birch reduction product $C_{60}H_{36}$.[14] After extremely long reactions, the most prominent peak corresponds to $C_{60}F_{46}$. At higher probe temperatures (400 °C) the C_{60}-rich samples gave peaks at $C_{60}F_{46}^+$, $C_{60}F_{48}^+$, $C_{60}F_{50}^+$, and $C_{60}F_{52}^+$.

MIKE (mass analyzed ion kinetic energy) and CAD (collisionally activated dissociation) spectra were run on several of the

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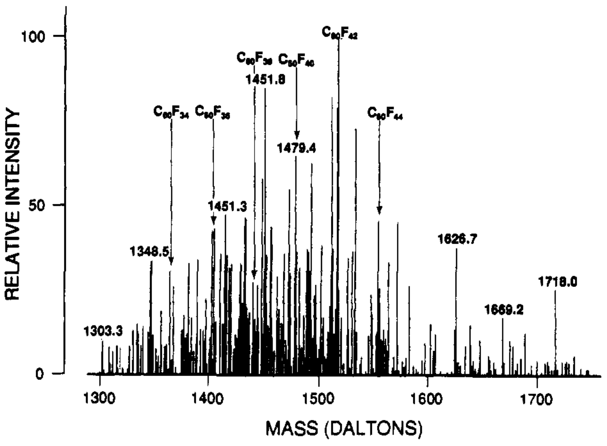

Figure 3. Field desorption mass spectrum of fluorinated C_{60} dissolved in C_6F_6. The spectrum is the sum of 22 aquisitions as the FD emitter current was increased from 0 to 28 mA. This increases the emitter temperature, driving off less-volatile species with increasing time.

major ions, including $C_{60}F_{2x}^+$ ($18 \leq x \leq 22$). No F_2 elimination was observed for any of these ions, showing that these are parent ions of the corresponding neutral fluorinated compounds. Fragmentation products such as $CF_3^{\bullet +}$ and $C_2F_5^{\bullet +}$ were observed. For example, a peak at 1435 D corresponds to the fragment $C_{59}F_{33}$ resulting from $CF_3^{\bullet +}$ loss from $C_{60}F_{36}$. The most intense peak in the C_{70}-rich spectrum is at 1752 D, corresponding to $C_{70}F_{48}^+$, although higher fluorinated products up to $C_{70}F_{52}^+$ were also present.

IV. Sublimed vs Crude Material

Attempts to isolate fluorofullerenes with specific n values using chromatographic procedures were unsuccessful. On the other hand, solid $C_{60}F_n$ was found to sublime under conditions similar to C_{60} and C_{70}, so separation was attempted by gradient sublimation using a dynamically-pumped vacuum system (primary vacuum with liquid nitrogen trap) described elsewhere.[18] With this system we can either scrape sublimed powder off the inner wall of the quartz tube or deposit fluorofullerene films directly onto suitable substrates. Source temperatures in the range 200–400 °C were tried, the best results being obtained by subliming at 300 °C for 24 h. Material deposited at the cold end was a uniform yellow solid. The nonvolatile residue was composed of a white powder mixed with black particles identified by electron diffraction as amorphous carbon. Higher source temperatures resulted in little deposition at the cold end, and the nonvolatile residue became grey in color. This material was mostly amorphous carbon. IR and UV–VIS of the residue and sublimate gave results similar to the crude product.

A field desorption mass spectrum (FD-MS) of the sublimate is shown in Figure 3. The major peaks and their assignments are 1518 D ($C_{60}F_{42}$), 1480 D ($C_{60}F_{40}$), and 1420 D ($C_{60}OF_{36}$). Weaker peaks represent other fluorinated compounds $C_{60}F_n$, where $n = 34$–44 is always an even number. Figure 4 presents logarithmic mass distributions of the crude material and sublimate, obtained by thermal desorption electron capture negative ion chemical ionization mass spectrometry, a technique which affords much better signal-to-noise ratio than FD-MS. Both samples show relatively broad distributions consisting of only even n species, with broad maxima centered around $n = 40$ and $n = 36$ for the crude material and sublimate, respectively. The crude material also shows a second distribution of heavier molecules extending from $n = 50$ all the way to $n = 60$, the $C_{60}F_{60}$ intensity being about 10^{-5} relative to the dominant $n = 40$ molecule. Macroamounts of fluorofullerenes with $n > 50$ are essentially absent from the sublimate. This could be attributed either to a lower volatility, in which case the higher fluorofullerenes should be found in the residue, or to the possibility that 300 °C is sufficient to cause liberation of F_2 (or CF_4) from the (presumably) less-stable higher fluorofullerenes. We believe the second hypothesis to be more likely, since mass spectra of the residue (not shown) showed no trace of species with $n \geq 50$.

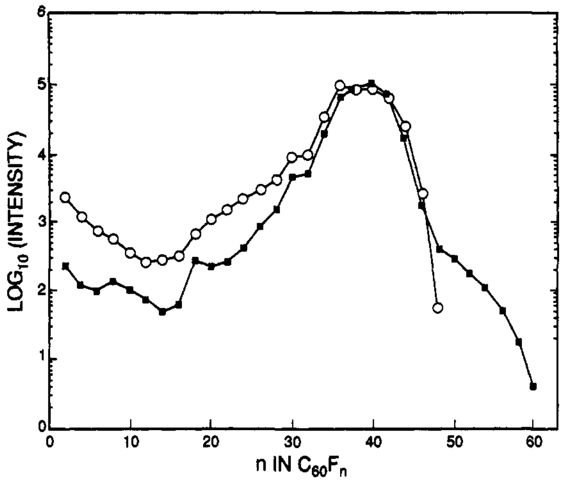

Figure 4. Comparison of high-sensitivity mass distributions (see text) of $C_{60}F_n$ crude fluorofullerenes (filled squares) and the sublimate (open circles).

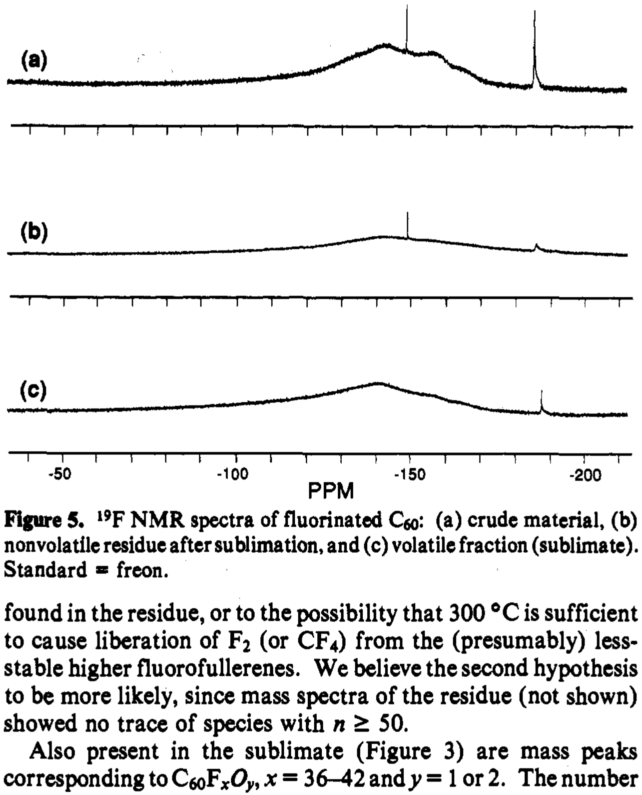

Figure 5. ^{19}F NMR spectra of fluorinated C_{60}: (a) crude material, (b) nonvolatile residue after sublimation, and (c) volatile fraction (sublimate). Standard = freon.

Also present in the sublimate (Figure 3) are mass peaks corresponding to $C_{60}F_xO_y$, $x = 36$–42 and $y = 1$ or 2. The number and intensity of these peaks suggests massive oxygen contamination, perhaps upon air exposure after sublimation or due to the gettering of residual gas during sublimation. We investigated the global oxygen content in sublimed films by means of Auger spectroscopy. No oxygen signal was observed above a level corresponding to a single oxygen atom per 100 atoms (e.g., in $C_{60}F_{40}$). We conclude that the as-sublimed material is essentially oxygen-free, and that the mass peaks due to oxyfluorofullerenes are somehow emphasized either by the mass spectrometric method or by extended air exposure.

^{19}F NMR spectra were obtained from crude fluorofullerenes, sublimate, and residue, by dissolving the respective powders in deuterated acetone and using freon as a standard, Figure 5. In all three samples, most of the nuclei are accounted for in broad features extending over a 200-ppm range and centered near −145 ppm. The crude product also reveals two prominent sharp peaks of comparable intensity at −149 and −188 ppm, Figure 5a. These have previously been assigned to $C_{60}F_{60}$ and HF, respectively,[5] the latter being attributed to HF liberated by reaction of fluorofullerenes with trace water. The −149 ppm peak is also present in the residue, Figure 5b, while the HF peak is considerably broadened (although the integrated intensities are again comparable). The −149 ppm peak is undetectable in the sublimed material, Figure 5c. At first glance this all seems consistent with the assignment of the −149 ppm peak to perfluorofullerene,[5] since our mass spectra showed no $C_{60}F_{60}$ in the sublimate. On the other hand, no perfluorofullerenes were detected in the mass spectrum of the residue either. In separate experiments we found that the intensity of the −149 ppm line reached a maximum well before saturation and then diminished with further F_2 uptake. We therefore suggest that the −149 ppm line results from some highly symmetric fluorofullerene other than $C_{60}F_{60}$, e.g., $C_{60}F_{36}$, and that its absence in the sublimate *dissolved in acetone* reflects the enhanced reactivity of sublimed material to nucleophilic substitution[6] which would destroy the high symmetry. It would thus appear that solid-state NMR will be necessary to "solve" the molecular structures of fluorofullerenes.

V. Reactivity

Fluorofullerenes are readily soluble in nonpolar (benzene and toluene) and polar (THF or acetone) solvents but do not dissolve in boiling water. To study the latter, we placed a few milligrams into a vessel with a magnetic stirrer. A yellow suspension was formed and did not dissolve after 24 h of continuous stirring. However when we added a few drops of THF a rapid exothermic reaction took place, as observed previously.[6] A similar reaction resulted from adding boiling water to an acetone solution. These observations are consistent with the nucleophilic substitution reaction proposed by Taylor *et al.*[6] Fluorofullerenes are thus strongly hydrophobic, and solvation or dissolution must occur before any reaction can take place. For this reason *solid* $C_{60}F_x$ is in fact quite stable and can be stored for at least months in air with no detectable changes in properties.

VI. X-ray Structure

We performed powder X-ray diffraction in order to obtain an approximate idea of the overall molecular structure and to find out if the differences in mass distributions between crude and sublimed materials, Figure 4, had any consequences on crystallinity. We used an INEL diffractometer equipped with a linear detector, fixed target X-ray generator utilizing the $\mathrm{Cu}_{K\alpha}$ line and a flat graphite monochromator. At room temperature, C_{60} molecules are orientationally disordered on a face-centered cubic lattice (fcc), with a lattice constant a = 14.17 Å, Figure 6a. Fluorinated pure C_{60}, Figure 6b, exhibits a few broad peaks characteristic of material with poor crystallinity but showing an obvious resemblance to pure C_{60} with a larger value of a, i.e., a nearest neighbor distance which has increased relative to pure C_{60}. The sublimate is much more crystalline, Figure 6c, sufficiently so that a Rietveld refinement became practicable, Figure 6d. The difference between data and fit for the sublimate is shown in the small bottom panel of Figure 6.

The refinement model is described as follows. The molecular form factor of orientationally disordered $C_{60}F_n$ molecules is represented as two concentric spherical shells, the smaller of which is composed of 60 carbons and is encapsulated by a larger one made up of a variable number of fluorines. Both shell radii are refineable parameters. Such "shell models" have been successfully applied in the analysis of the plastic crystal phase of pristine C_{60}.[16] Peak positions and systematic absences suggested a hexagonal close packed lattice (hcp), but the observed intensities were very poorly reproduced by models in which the stacking of close-packed molecular layers was restricted to ABAB (goodness of fit parameter $\chi^2 > 60$). Thus a variable fraction of molecules was allowed to occupy an fcc lattice which, sharing the same close packed planes as hcp, has the same peak positions for hcp basal plane scattering. This improved the fit dramatically (weighted $\chi^2 \approx 4$, see difference plot and Figure 6d).

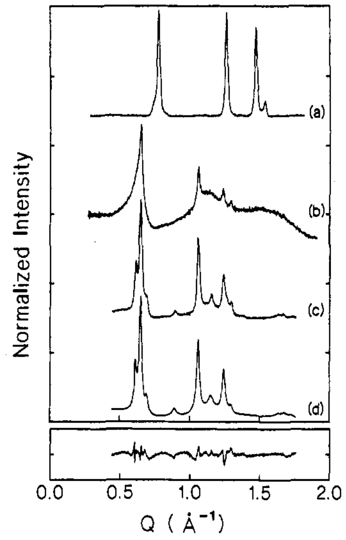

Figure 6. Powder X-ray diffraction profiles: (a) pure C_{60}, (b) crude fluorofullerenes, (c) sublimed fluorofullerenes, and (d) best fit to (c) using model described in the text. Bottom panel: difference between data (c) and fit (d).

Table I

sample	contact angles max.	min	av[a]
Si(100) wafer	39	32.5	36 ± 2 (10)
$C_{60/70}$	73.5	63	70 ± 2 (13)
$C_{60}F_{47}$	93	87	89 ± 2 (10)
Teflon	106	80	95 ± 6 (13)

[a] Numbers in parentheses are number of measurements.

In the final optimized refinement, the majority (60%) of fluorofullerenes were found to be in the fcc phase, with a(fcc) = 16.677 Å. The corresponding hcp lattice parameters were a(hcp) = 11.85 Å and c = 19.28 Å. Note that c/a(hcp) = 1.627 and a(fcc) is nearly equal to a(hcp) × $\sqrt{2}$ = 16.758 Å, indicating that in both phases the molecules pack as spheres of equal average diameter. The coexistence of ABAB and ABC stacking sequences resembles the problem encountered in pure C_{70}.[17] However, in contrast to C_{70}, sublimed fluorofullerenes remain as a mixture of fcc and hcp even after extended annealing. The optimized value for the average $n = F/C_{60}$ is 47 ± 5, in good agreement with weight uptake. The average C–F bond length inferred from the difference in shell radii is 1.49 Å (fullerene cage radius 3.51 Å, the same as in pure C_{60};[16] fluorine cage radius 5.00 Å). This differs from the 1.35 Å value deduced from core level photoemission spectra of $C_{60}F_{48}$ films sublimed *in situ*.[10]

It was somewhat surprising to us that solid fluorofullerenes crystallize at all, given the broad distribution of molecular weights present. The intermolecular bonding in solid C_{60} is essentially van der Waals,[15] but the fact that all the randomly-oriented molecules are precisely the same size allows for a high degree of positional order, with X-ray coherence lengths approaching 1 micron in our best powder samples. The fact that fullerenes and fluorofullerenes sublime under similar conditions suggests that the intermolecular bonding strengths are also similar, so the obviously poorer crystallinity must be connected to a distribution of molecular radii implied by the distribution of F/C_{60} ratios. But the size distribution must be a lot narrower than the F/C_{60} distribution. A possible explanation for the substantial crystallinity observed in the sublimate is that the fluorofullerenes are randomly oriented on the X-ray time scale similar to C_{60}, such that their effective radii are determined mainly by the C–F bond length while the F/C_{60} distribution has only a minor influence.

For this to be the case, the much poorer crystallinity of the crude material would have to be attributed to the presence of only a few percent of fluorofullerenes with $n > 50$, this being the only apparent difference between crude and sublimed materials. Indeed the lattice parameters of the crude material (obtained from the positions of the few broad reflections, Figure 6b) closely match the refined values for the sublimate, suggesting that the major effect of the higher fluorofullerenes is to introduce additional positional disorder rather than to dilate the lattice. Resolution of these issues must await the availability of single-species samples.

We used high-temperature X-ray diffraction in an attempt to determine the melting point of the sublimate. In contrast to Taylor *et al.*,[6] we did not observe any sign of melting up to 300 °C. We did however find evidence for additional fluorine loss from the sublimed material, as manifested by considerable darkening from light yellow to dark yellow/brown in the course of the X-ray experiments. This color change was *not* accompanied by any measurable changes in X-ray peak intensities or widths. Similarly, we found that the X-ray profiles of the crude material and the residue after sublimation were similar despite their quite different visual appearances.

VII. Contact Angle Measurements

We have also made preliminary measurements on thin films of fluorofullerenes, the results of which are indirectly related to potential lubrication properties. We determined surface tensions by measuring contact angles with water droplets. Films of pristine fullerenes (mixtures of C_{60} and C_{70}) and their fluorinated derivatives were prepared by spin-coating toluene solutions onto Si(100) wafers at 1500 rpm.[19] Contact angle measurements were done on a Rame-hart Contact Angle Goniometer (Model 100-11). Water droplets were dispensed with a microsyringe attachment (Model 100-10). Contact angles were measured on both sides of the droplets and averaged. Measurements were performed by two observers to minimize subjective errors. The results are summarized and compared with those obtained from a smoothly machined Teflon block in Table I. The results indicate that fluorinated fullerenes show about the same contact angle as Teflon but higher than that of pristine fullerene. The Teflon values scatter considerably, possibly because of the difficulty of obtaining a perfectly smooth surface. Thus, the measurement may depend to some extent on the location of the drop on the Teflon surface, a problem not encountered with the cast films.

VIII. Conclusions

The reaction of fullerenes with elemental fluorine produces fluorinated compounds with stoichiometries ranging from $C_{60}F_{30}$ to $C_{60}F_{52}$, with $C_{60}F_{36}$ being particularly stable. A similar range of fluorinated compounds is obtained with C_{70}. The most challenging task is not the synthesis itself but separation of the product. A partial separation is possible by sublimation of the crude product. The volatile fraction (sublimate) is composed mostly of $C_{60}F_{42}$ and $C_{60}F_{40}$ and has a better-defined crystal structure than the crude material. Mass spectrometry and X-ray results show that crystalline fluorofullerenes do not contain the most highly fluorinated species. The 1.49 Å carbon–fluorine bond length inferred from X-ray analysis is longer than the *ca.* 1.3 Å typical of perfluoroalkanes. Therefore the chemical stability of fluorofullerenes should be weaker than fluoroalkanes, which agrees with the findings of Taylor *et al.*[6] as well as with ours. We have also found that $C_{60}F_{60}$ indeed exists, but with an intensity of only 1 part in 10^5 relative to the dominant species. In a very recent report, Tuinman *et al.* observed a much larger fraction, *ca.* 1 part per 100, in a fluorinated sample subjected to a second fluorination under UV irradiation.[22] But their series of mass peaks extends well beyond $n = 60$ to $C_{60}F_{76}$, leading to the proposal of "hyperfluorination" in which one or more of the 90 σ bonds on a buckyball has been disrupted in some manner. More work is clearly called for on this novel family of fluorocarbon compounds.

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