Hyperfluorination of [60]fullerene by krypton difluoride

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Mass spectroscopy of the product of [60]fullerene fluorination by KrF_2 in HF, shows the most abundant species present to be $C_{60}F_{44}$ and $C_{60}F_{46}$; cage-opened compounds with molecular formulae up to $C_{60}F_{78}$ are also present. Despite long exposure of the samples to air prior to analysis, oxygenated derivatives (containing one or two oxygen atoms) are present in low concentration only. The ubiquitous oxygen content of fluorofullerenes does not therefore appear to arise substantially from atmospheric contamination. The EI mass spectrum differs from that obtained with F_2-fluorinated [60]fullerene in showing a greater concentration of fragmentation ions, including species of even mass; these latter may arise from cage-opened species. The ^{19}F NMR spectrum of the product (tetrahydrofuran solution) is similar to that found with F_2-fluorinated material, and in particular shows the sharp singlet at *ca.* 151 ppm, attributed previously to a symmetrical species such as $C_{60}F_{60}$. With aqueous methanol, significant reaction does not occur, in marked contrast to the behaviour of fluorine-gas fluorinated [60]fullerene; possible reasons for this difference are considered.

Fluorination is of considerable interest in fullerene chemistry, because of the perceived value of the products in materials science. Progress in this area is however hampered by the difficulty of either isolating single components or in controlling the fluorination reaction. For example, fullerenes containing only a few fluorine atoms have not been isolated, though recently one of us has obtained evidence that such species have real existence rather than arising merely from fragmentation during mass spectrometry.[1] In view of the many papers now published on fullerene fluorination, it is appropriate to summarise the main observations to date.

(*i*) The fluorinated products are very soluble in polar solvents.

(*ii*) The mass spectra of the products have a maximum intensity around $C_{60}F_{46}/C_{60}F_{48}$.[2–7]

(*iii*) Fluorinated species up to $C_{60}F_{60}$ have been detected in fluorination by F_2 gas,[5,7] and hyperfluorinated species up to $C_{60}F_{76}$ have been detected by fluorination with F_2 under UV irradiation.[6]

(*iv*) Oxygenated species are present. Those containing up to 11 oxygen atoms have been observed in the products of fluorination of [60]fullerene by fluorine gas.[2,8] The oxygen is believed to be present as the epoxide, and together with the fluorine present, accounted for up to 58 site occupancies from various $C_{60}F_xO_y$ combinations. Other workers have reported mass spectroscopic evidence for the presence of up to five oxygen atoms,[5] the various $C_{60}F_xO_y$ combinations here (*e.g.* $C_{60}F_{48}O_5$, $C_{60}F_{50}O_4$, $C_{60}F_{56}O$) corresponding also to a maximum of 58 site occupancies. Fluorohalo derivatives of [60]fullerene resulting from reaction with either ClF_3 or BrF_5 have been inferred to contain up to 12 oxygen atoms.[7] The source of these oxygen atoms is unclear,[9] though it has been shown that the concentration and number of these species can be increased by reaction with aq. methanol, whereby nucleophilic substitution of F by OH followed by *cis* elimination of HF is thought to occur.[2,8,10] In the present work we provide further evidence concerning these oxygenated species.

(*v*) Efforts to separate the oxygenated materials by sublimation have been inconclusive. Whilst sublimation causes loss of species $C_{60}F_{>48}$ indicating that they have lower stability (which would follow from steric congestion), it was reported to produce no change in the concentration of oxygenated species,[5] though a later report by the same group stated that a reduction in oxygen content resulted.[11] Sublimation also caused a change in the species of maximum ion intensity in the mass spectrum,[5] from $C_{60}F_{40}$ to $C_{60}F_{36}$ (which may suggest that degradation occurs during mass spectrometry). Heating of fluorinated [60]fullerene [deposited on a KBr plate from tetrahydrofuran (THF) in *vacuo* at 80 °C caused a change in the IR spectrum, and a decrease in solubility of the product.[2]

Experimental

The fluorinated samples were prepared according to established fluorinating procedures,[12] at the Kurchatov State Scientific Centre, Moscow, Russia, and were kindly donated by Dr V. B. Sokolov. [60]Fullerene (99.9%) was fluorinated in a Teflon mini reactor with KrF_2 in anhydrous HF with constant stirring at room temperature during two days, after which no further increase in weight was observed. The yellow product turned white after heating *in vacuo* at 150 °C during 10 min. Full details, including fluorination of [70]fullerene under the same conditions, will be published by the Russian group in due course.

The ^{19}F NMR spectrum was obtained on a solution of the fluorofullerene in THF. EI mass spectra were obtained on solid samples introduced into the mass spectrometer in a capillary tube with temperature ramping from 30 to 500 °C. The spectrometer was a VG Analytical double-focussing, normal geometry instrument, operated at 70 eV, 8 kV accelerating voltage, calibrated from 20 to 3000 amu, with data acquired at 3 s per decade, 1 s delay between scans; the temperature of the ion source was constant at 250 °C.

Methanol was added to samples of the fluorofullerene and allowed to stand overnight for solution to occur. The methanolic solution was added to a DCI probe and the solvent allowed to evaporate before the probe was introduced into the mass spectrometer. The probe temperature was ramped up to 500 °C.

Results and discussion

Occurrence of hyperfluorinated species

Fig. 1 shows the mass spectrum of the white sample with (inset, right) the region from 1650–2250 amu expanded. The peak intensity maximum occurs at $C_{60}F_{46}$; in the more yellow sample this occurred at $C_{60}F_{44}$. Species up to $C_{60}F_{78}$ are evident. This

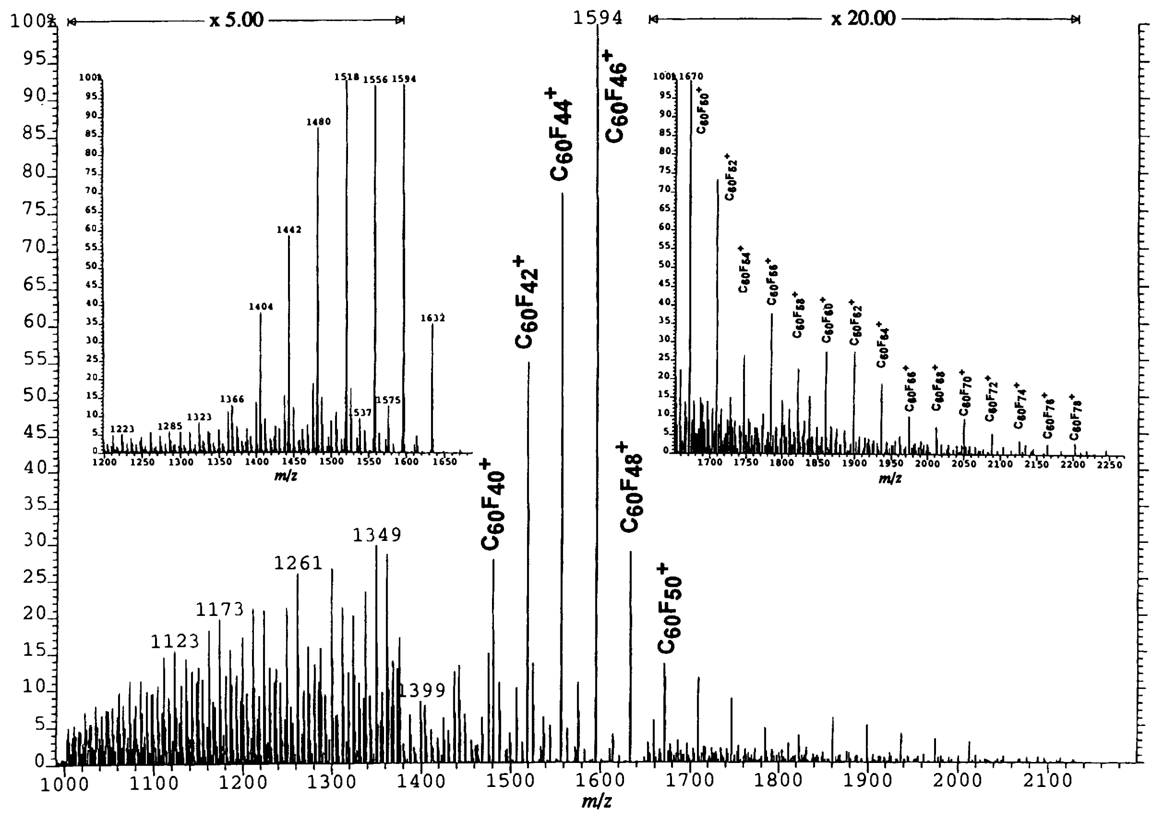

Fig. 1 Mass spectrum (EI) of KrF_2-fluorinated [60]fullerene (white sample). Inset (right) is expansion of the region of highly fluorinated material. Inset (left) is the sample after reacting with aq. methanol. Intensity amplifications (Figure top) refer to the main spectrum.

result may be compared with those of Tuinman *et al.*[6] who found under their hyperfluorination conditions, a peak intensity maximum at $C_{60}F_{48}$, with species up to $C_{60}F_{76}$ present.[6] There is evidently a parallel between the two sets of work, despite the different reaction conditions. Both works show a marked decrease in ion intensity above $C_{60}F_{48}$, and this has been attributed to the more highly fluorinated species being cage-opened ones.[6] This may not necessarily follow because steric congestion in the more highly fluorinated species can cause a decrease in stability below the point at which thermal elimination readily occurs, hence these ions are absent or of low intensity in the mass spectrum. Evidence below suggests that this indeed occurs.

Fragmentation ions

Fig. 2 shows part of the low mass region of the spectrum (white sample) which is dominated by odd-mass fragmentation species, *viz.* $C_{52}F_{21-27}$, $C_{53}F_{21-29}$, $C_{54}F_{21-33}$, $C_{55}F_{23-33}$, $C_{56}F_{21-37}$, $C_{57}F_{23-39}$, $C_{58}F_{23-41}$, $C_{59}F_{29-45}$ and $C_{60}F_{35-47}$. Many are identical to those which have been observed before,[8] but in the present case more species are found, indicating that greater fragmentation is occurring with the more highly fluorinated material. In contrast to results obtained with less highly fluorinated material,[8] there are also a large number of even mass fragmentation ions present *viz.* $C_{56}F_{18-38}$, $C_{57}F_{26-36}$, $C_{58}F_{34-38}$ and $C_{59}F_{36-40}$. One possible explanation is that a significant pathway for decomposition involves loss of CF_3,[4,8] as well as F and CF_2;[8] loss of CF_2 is very evident in the spectrum (as in previous ones)[8] in the series of ions showing 50 amu loss from m/z = 1373 ($C_{59}F_{35}$) down to 1023 ($C_{52}F_{21}$), and 1361 ($C_{58}F_{35}$) down to 1011 ($C_{51}F_{21}$). A closed cage species will always have an even number of fluorines present (as C–F groups) and loss of either F or CF_3 followed by CF_2 will result in an odd mass fragment. An open cage species must have present initially some CF_2 groups, which may thus be lost preferentially thereby retaining an even mass. The difference in the fragmentation patterns of fluorinated fullerenes may thus serve as an additional indicator of the occurrence of hyperfluorination, especially as the hyperfluorinated species are likely to be more unstable under mass spectroscopic conditions.

Presence of oxides

Ions due to oxides are present in the spectra [in particular $C_{60}F_nO$ (n = 18–32)] but the yields are low which contrasts markedly with material that has been fluorinated by fluorine gas. Material that was heated under vacuum at 70 °C for 3 h, showed a significant reduction in the concentration of oxides (see Fig. 3 and inset), indicating either that they are more volatile or that they de-oxygenate on heating.

The concentrations of the oxygenated species increases with decreasing fluorine content, which would be consistent with the nucleophilic substitution/*cis* elimination mechanism described above. It is noteworthy that the samples were exposed to air for *ca.* 4 weeks prior to being analysed, yet the oxide content is much lower than that for samples fluorinated with fluorine gas and kept under nitrogen prior to analysis. This suggests that the oxides are not produced from reaction with atmospheric oxygen. It may however be the case that reaction with atmospheric water traces may take place at quite different rates depending upon the condition of the fluorinated material, in turn dependent upon the fluorination method. Firm evidence to support this view was provided by the action of methanol. Most surprisingly, this produced almost no change in the concentration of oxygenated species in the spectrum (Fig. 1 inset left). This contrasts with the behaviour of material fluorinated by fluorine gas; a fresh batch provided by Professor J. H. Holloway behaved exactly as reported previously.[2,8]

It is presently unclear as to why material from two different fluorinating procedures behave so remarkably differently. One possibility could be that the hyperfluorinated material is sub-

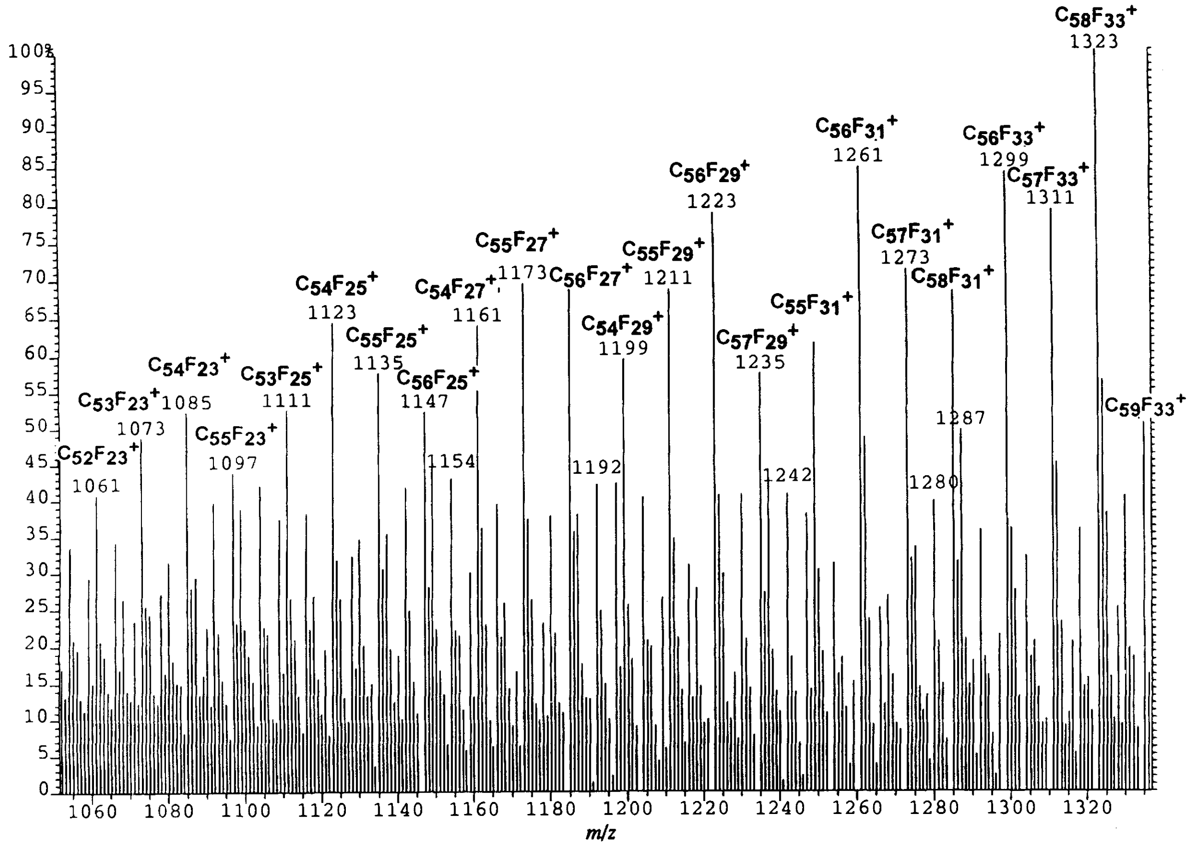

Fig. 2 Mass spectrum (EI) of part of the fragmentation ion region of Fig. 1, with some major peaks indicated

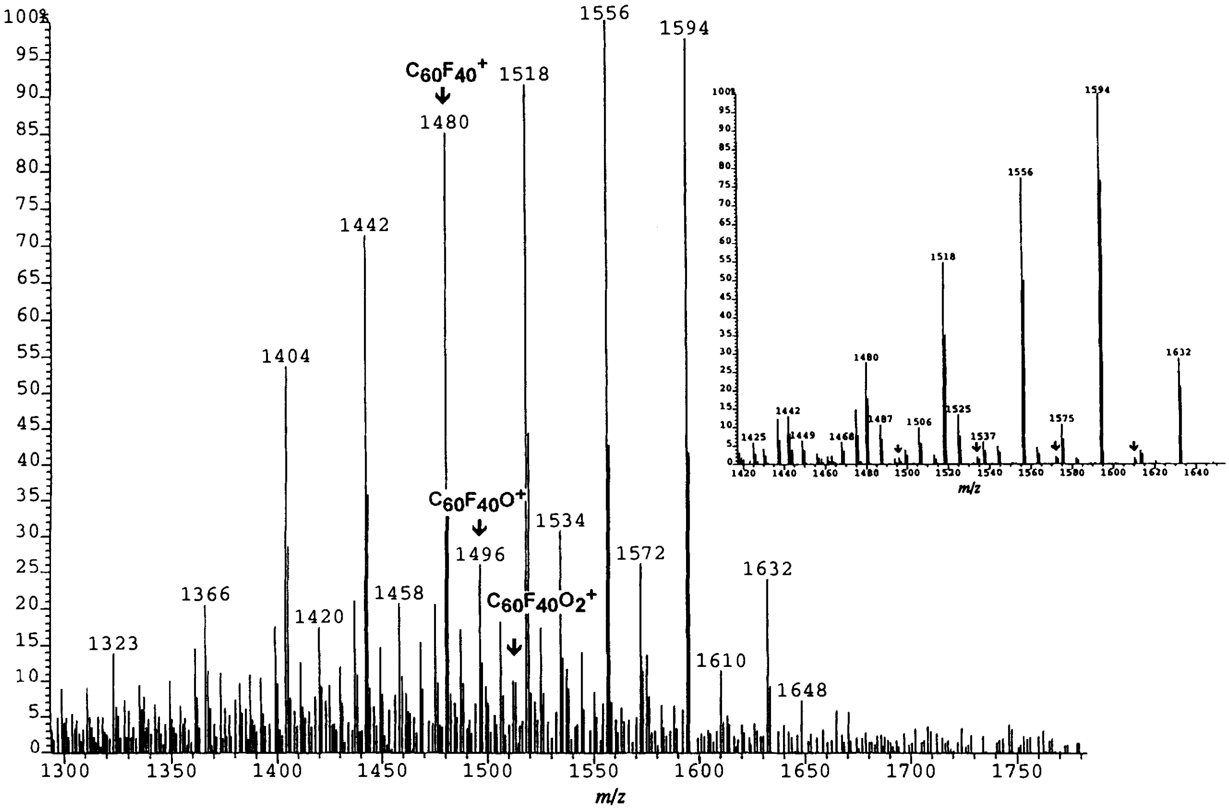

Fig. 3 Mass spectrum of KrF_2-fluorinated material (yellow sample), showing relatively low concentrations of oxygenated species (two are highlighted). Inset shows the same material after gentle heating as described in the text. Residual traces of oxygenated material are indicated by arrows.

stantially cage-opened, so that the driving force for nucleophilic substitution, so marked with fullerenes and the fluorofullerenes in particular[10] is lessened. However, this implies that the mass spectra are unrepresentative of the true composition of the material due to degradation. Another conjecture also requires that the cage be largely fully fluorinated, since the nucleophilic substitution mechanism (which has been proposed as being of the addition–elimination type[2,10]) cannot then occur because this process requires the presence of at least one vacant double bond on the cage. The difference in the two kinds of material is clearly of great importance in view of the possible uses of fluorofullerenes. We hope to investigate this aspect in greater detail once additional supplies of the KrF_2-derived material become available.

Stabilities of the fluorinated species

In a previous publication we noted that $C_{60}F_{18}O$, $C_{60}F_{18}O_2$ and $C_{60}F_{36}O$ gave greater ion intensities in some mass spectra of fluorinated [60]fullerene.[8] A similar result has been noted for $C_{60}F_{18}$ and $C_{60}F_{18}O$ by Chowdhury *et al.*,[5] as well as the sudden increase in stability around $C_{60}F_{36}$, which is evident in the present work too. There is thus a parallel with the results for hydrogenation where species containing 18 and 36 hydrogens are particularly stable.[13] One of us proposed earlier that the stability of $C_{60}H_{36}$ arose from its *T* symmetry (containing four highly delocalized benzenoid rings),[14] and this has since been supported by many calculations.[15] A similar explanation appears to account for the stability of $C_{60}F_{36}$. Hydrogenation stops at the 36 addend stage because the activation energy for further hydrogenation is very high. However, this is not the case for fluorination and so further reaction takes place, with further fluorines being added. One would expect that the structures of the more fluorinated material would reflect the $C_{60}F_{36}$ precursor, but this is apparently not the case for $C_{60}F_{48}$.[16] [There are however, unexpected aspects of the ^{19}F NMR spectrum used to assign this structure, each of the b/e, d/e, e/g and f/h couplings (see original paper for notation) being absent.] If the structure is confirmed, it suggests that further fluorine addition is accompanied by fluorine migration over the surface of the cage.

^{19}F NMR spectrum

The ^{19}F NMR spectrum for fluorinated [60]fullerene was first reported in 1991,[17] a distinct characteristic being a sharp singlet at δ −150.5 sometimes accompanied by a second singlet at δ −152.7. This indicated the presence of a highly symmetrical species such as $C_{60}F_{60}$. Other workers have obtained similar NMR spectra.[18] We now find similar spectra from the hyperfluorinated samples, but there is a definite variation according to the quality of the THF solvent used. Fig. 4(*a*) shows the spectrum obtained with a sample in reasonably dry THF: the sharp singlet is evident at *ca.* δ −151 together with the usual peak for HF at δ −187.5. On addition of water, the spectrum (not shown) is virtually unchanged, except that the peak for HF moves downfield to δ −184.7 due to hydrogen bonding, as noted previously for F_2-fluorinated material.[10] However, the spectrum obtained in freshly dried THF [Fig. 4(*b*)] has different characteristics. The quality of the solvent is indicated by the upfield position of the HF peak at δ −193.8 and the singlet in the δ −151 region is now replaced by two much smaller ones (δ −151.0, −151.3). We cannot discount at this stage the possibility that peaks in this region arise from an unknown reaction between the fluorinated material and the solvent. A mass spectrum of material that had been standing for a few days with THF showed that polymerization of the ether occurs, with peaks appearing at 71, 141, 211, 279, 350 and 420 amu. Previously, acetone was found to undergo aldol-condensation by HF arising from reaction of the fluorofullerene with water traces in the solvent,[17] and it seems probable that a similar explanation accounts for the present results.

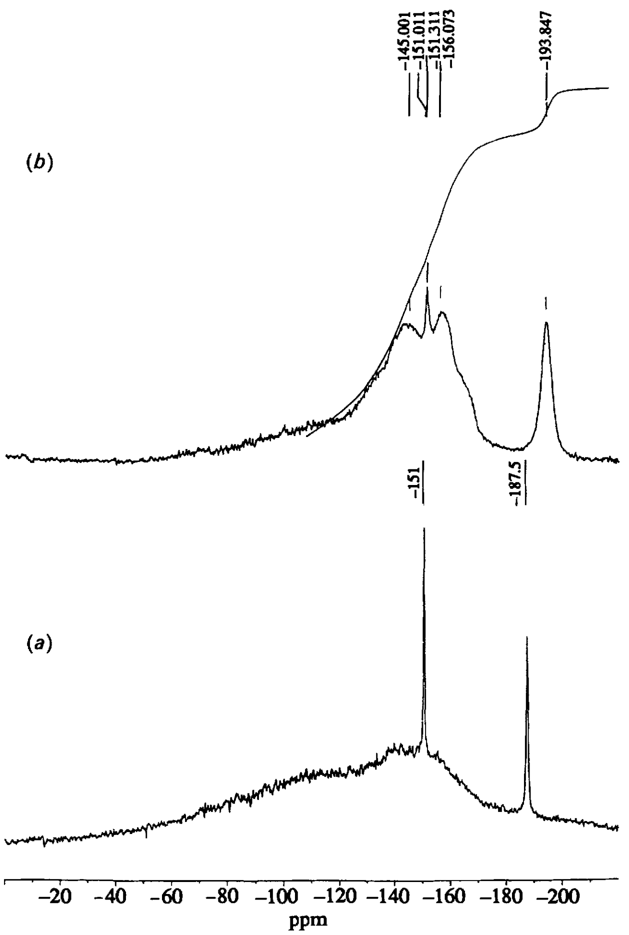

Fig. 4 ^{19}F NMR spectrum of KrF_2-fluorinated material (white sample), in dry THF (below) and freshly dried and distilled THF (above)

Further work in collaboration with Professor J. H. Holloway on the behaviour of F_2-fluorinated material in different solvents is in hand.

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