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In situ synthesis and characterization of fullerene derivatives by Knudsen-cell mass spectrometry

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Dedicated to Prof. Helmut Schwarz on the occasion of his sixtieth birthday

Abstract

The use of a mass spectrometer equipped with a Knudsen cell *as a chemical reactor* for studies of solid-state reactions of fullerenes is described. The simultaneous generation and mass-spectrometric detection of the volatile products provided a wealth of information on the dynamics of formation and the distribution of products as reaction conditions were varied in each synthesis/characterization experiment. A combination of new results and previously published data are used to demonstrate how in situ Knudsen-cell mass spectrometry led to the rapid development of an important branch of synthetic fullerene chemistry that has yielded many new fluorofullerenes and related derivatives with novel structures and properties.

Keywords: Knudsen-cell mass spectrometry; Fullerenes; Fluorination; Transition metal fluorides; Trifluoromethylation

1. Introduction

Studies of large clusters by mass spectrometry are generally considered a bridge between gas-phase chemistry and solid-state or solution chemistry. One can hardly find a better illustration of the seminal role of mass spectrometry in a significant new field of condensed-phase chemistry than the discovery of fullerenes.

In 1985, scientists from Rice University, USA, and Sussex University, UK, observed the abundant presence of large carbon clusters in laser-desorbed vapors of graphite and predicted the nearly spherical structure of one of them, a 60-carbon-atom cluster that they named Buckminsterfullerene [1]. Fullerenes remained the exclusive domain of gas-phase spectroscopists and theorists for several years, until Krätschmer et al. detected fullerenes in carbon soot produced by the arc-discharge method and developed the method of macroscopic preparation of fullerenes [2].

A decade later, mass spectrometry continues to play a significant role in the development of the chemistry of fullerenes. For example, there are many more mass-spectrometry determined ionization energies and electron affinities of fullerenes and their

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Abbreviations: ISKC, in situ Knudsen cell; SBG, small bandgap; AgTFA, silver(I) trifluoroacetate; HPLC, high performance liquid chromatography

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derivatives [3,4] than solution-electrochemistry determined redox potentials [5], and the gas-phase values have proven useful to synthetic chemists in choosing reagents and conditions for the further elaboration of fullerene derivatives. This is because there is a strong correlation between the few known redox potentials and their equivalent gas-phase values.

Another example is the remarkable discovery by Schwarz and co-workers that collisions of C_{60}^{+} and helium atoms result in the formation of He@C_{60} [6]. The elegant proof in Schwarz's paper of the endohedral nature of the helium atom was later confirmed when solid samples containing small amounts of He@C_{60} were prepared from C_{60} and helium at high temperature and pressure [7].

An additional example of the impact of mass spectrometry on the synthesis of fullerene derivatives, specifically the synthesis of fluorinated fullerenes (fluorofullerenes), is the subject of this paper. We will describe how our group used a magnetic-sector mass spectrometer equipped with a Knudsen effusion cell in a nontraditional way, *as a chemical reactor*. Solid-state reactions of fullerenes with various transition-metal and rare-earth-metal fluorides as fluorinating reagents or with the trifluoromethylating reagent silver(I) trifluoroacetate (AgTFA) were carried out in the Knudsen cell. The simultaneous generation and mass-spectrometric detection of the volatile products provided a wealth of information on the dynamics of formation and the distribution of products as reaction conditions were varied in each synthesis/characterization experiment. Significantly, a large fraction of the products could be condensed on a specially designed collection plate, which allowed for the further spectroscopic characterization of the new derivatives. This technique was largely responsible for the rapid development of synthetic fluorofullerene chemistry. By learning from the mass spectrometrists which reagents and conditions would lead to which fluorofullerene compositions, synthetic chemists can now prepare macroscopic amounts of many new fluorofullerenes and related derivatives with novel structures and properties [8,9].

2. Experimental

2.1. In situ Knudsen-cell synthesis and mass spectrometry

A commercial MI 12 01 (USSR) magnetic-sector mass spectrometer was equipped with a Knudsen cell assembly designed and fabricated at Moscow State University. Ionization was achieved using high-energy

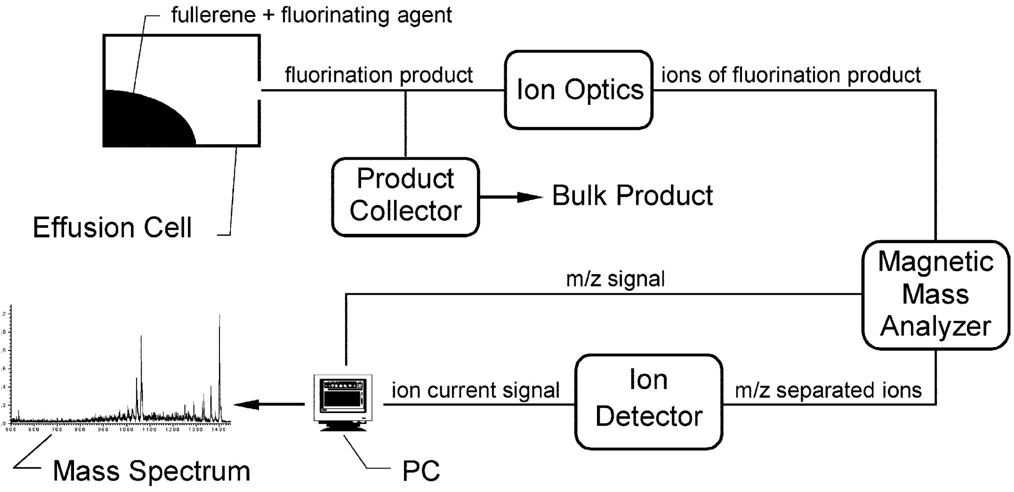

Fig. 1. Schematic drawing of the experimental setup for simultaneous in situ Knudsen-cell synthesis (fluorination) and mass spectral characterization of fullerenes.

electrons (70–150 eV). The accelerating voltage was set at 1.38–2 kV, which allowed for coverage of the mass range up to 2000 Da. The effusion cell (Ni) was resistively heated (200–600 °C); its temperature was measured using a calibrated Pt/Pt–Rh thermocouple with an accuracy of ±2 °C. A collection plate (Ni) was used to condense the gas-phase products evaporating from the cell; it was placed between the ion optics and the sample evaporator. A schematic of the experimental setup is shown in Fig. 1.

2.2. Materials

The compounds MnF_3 (Aldrich), AgF (Lancaster) and C_{60} and C_{70} (Term USA) were used as received. AgTFA was prepared by treating silver(I) oxide with a 0.5 M aqueous solution of trifluoroacetic acid. Following recrystallization from water, the purified AgTFA was characterized by X-ray powder diffraction and infrared spectroscopy.

The other reagents used in this work were obtained from the indicated collaborators, who prepared and purified them as described in the indicated references: C_{76} and C_{84} (Darwish, Sussex University [10]); C_{74} (Bolskar, TDA Research Co. [11]); $(C_{59}N)_2$ (Hirsch, Friedrich-Alexander Universität [12]); CeF_4, K_2PtF_6, and K_3CoF_6 (Polyakova, Inst. of Electrocarbon Materials; these compounds were characterized by the authors using X-ray powder diffraction and elemental analysis); and AgF_2 (Žemva, Josef Stefan Inst. [13]).

3. Results and discussion

3.1. Selective fluorinations of [60]fullerene

3.1.1. $C_{60}F_{36}$

Manganese(III) fluoride (MnF_3) was the first fluorinating reagent used successfully for the in situ Knudsen-cell (ISKC) fluorination of C_{60} in a mass spectrometer [14]. A series of experiments performed at 300–500 °C with various C_{60}/MnF_3 ratios showed that $C_{60}F_{36}$ was the main product, with only a few percent of several impurities including $C_{60}F_{34}$, $C_{60}F_{34}O$, $C_{60}F_{36}O$ and $C_{60}F_{38}$. Subsequent EI mass spectral analysis of the powdered material collected from the cold parts of the ion source after completion of the reaction precisely reproduced the results obtained during the in situ experiments [15].

The significance of this finding was far beyond the satisfaction of knowing that the calibration of our instrument in the high mass region was accurate. It provided us with the following crucial information about the behavior of fluorinated fullerenes:

(i) they are thermally stable, since vacuum resublimation did not result in a change in composition of the mixture;
(ii) they do not fragment under EI conditions (i.e., molecular ions dominated the mass spectra), which permitted an accurate estimation of the relative amounts of the products generated in the in situ experiments (the main fragmentation channels were CF_3 loss (ca. 3–5% of the molecular ion intensity) for the higher fluorinated fullerenes (i.e., $C_{60}F_{36–48}$) and F atom loss (ca. 10–15%) for the lower fluorinated species (i.e., $C_{60}F_{2–18}$));
(iii) their volatilities are considerably higher than C_{60} and the metal fluoride fluorinating reagents, which affords a "clean" synthesis (i.e., by choosing appropriate reaction conditions it was possible to obtain fluorofullerenes without any trace of the starting materials);
(iv) they can be prepared virtually free of previously reported [16] oxygenation products as long as the reactions are carried out under high vacuum;
(v) most importantly, some fluorofullerenes can be prepared with 90+% compositional purity (up until that time, fluorofullerenes had only been prepared as complex mixtures, and the highest reported compositional purity for a fluorofullerene was 69% for $C_{60}F_{48}$ [17]).

These serendipitous findings encouraged us to probe other solid fluorinating agents in our ISKC experiments. The results of these experiments guided our future synthetic strategy for the preparation of macroscopic amounts of selected fluorofullerenes.

The key role of the mass spectrometer—not as a routine analytical instrument but as a unique tool for determining *and controlling* the distribution of products in real time during the fluorination reactions—cannot be overestimated. The correspondence of gas-phase compositions with the distribution of molecules in the isolated solid product was a breakthrough discovery. The immediate evaporation of volatile, selectively fluorinated fullerenes from the effusion chamber of the mass spectrometer (i.e., from the reaction zone) indicated how to carry out these reactions on a larger scale so that the products would not need to be separated from the starting materials. In addition, even the choice of particular metal fluorides for the ISKC experiments was facilitated by mass spectrometry in that it was based on our previous mass spectral determination of M–F bond dissociation energies of transition-metal fluorides [18], which are correlated with the relative fluorinating abilities of the various MF_n compounds [13].

3.1.2. $C_{60}F_{18}$

The fullerene C_{60} reacted differently with K_2PtF_6 at 320–500 °C than it did with MnF_3. The product $C_{60}F_{36}$ was only observed at the initial stage of the reaction. The bulk of the product after the initial stage consisted of a specific fluorofullerene with half the number of fluorine atoms per C_{60} molecule, i.e., $C_{60}F_{18}$! This result was later confirmed by HPLC analysis of an isolated batch of the product, which showed predominantly $C_{60}F_{18}$ with much smaller quantities of $C_{60}F_{36}$ and fluorofullerenes with fewer than 18 fluorine atoms [19]. Structural characterization by NMR spectroscopy [19] and single-crystal X-ray diffraction [20] revealed a single isomer of $C_{60}F_{18}$, which has a remarkable crown-like structure with all 18 fluorine atoms located on one hemisphere of the fullerene. Consequently, $C_{60}F_{18}$ is a very polar molecule (the estimated dipole moment of $C_{60}F_{18}$ is 6–8 D [21]).

Based on the ISKC experiments just described, a relatively simple high-temperature evacuable glass reactor was fabricated at MSU in order to scale up the syntheses. The results proved that the in situ mass spectrometric syntheses could be reproduced on a much larger scale. For the first time, *hundreds of milligrams* of the fluorofullerenes $C_{60}F_{36}$ ($C_{60} + MnF_3$) and $C_{60}F_{18}$ ($C_{60} + K_2PtF_6$) were obtained with 90+% compositional purity from a one-step reaction followed by simple vacuum-sublimation purification [22]. The isolated $C_{60}F_{36}$ was found to be a mixture of isomers (the two major isomers were found to have C_3 and T symmetries [23]). The compound $C_{60}F_{18}$ was isolated as a single isomer.

The ISKC fluorination of C_{60} with CeF_4, as well as the subsequent bulk synthesis in the evacuable glass reactor, demonstrated that CeF_4 and MnF_3 are equally competent as selective reagents for the formation of compositionally pure $C_{60}F_{36}$. In contrast, CoF_3 produced a complex mixture of molecular species more highly fluorinated than $C_{60}F_{36}$ and therefore is unsuitable for the selective fluorination of C_{60}.

3.1.3. $C_{60}F_{44}$

When C_{60} was treated with AgF_2 at 300 °C in the Knudsen cell, the mass spectrum (Fig. 2) was essentially that of a single species, $C_{60}F_{44}{}^+$, during the entire course of the reaction. The loss of $CF_3{}^\bullet$ or $C_2F_5{}^\bullet$ fragments from $C_{60}F_{44}$ was negligible (as previously observed for $C_{60}F_{48}$ [24]); the parent ion $C_{60}F_{44}{}^+$ was responsible for 95+% of the total mass spectral intensity.

The reactive compound AgF_2 is very sensitive to storage conditions and readily degrades if not handled properly by experienced personnel. By trial and error, we learned that even slightly degraded samples of AgF_2 resulted in a significant loss of selectivity. Instead of relatively pure samples of $C_{60}F_{44}$, we observed a broad distribution of products from $C_{60}F_{36}$ to $C_{60}F_{44}$ that had a maximum EI mass-spectral intensity for either $C_{60}F_{36}$ or $C_{60}F_{38}$. In contrast, the use of slightly hydrolyzed samples of MnF_3 resulted only in a decreased yield of $C_{60}F_{36}$ but not in a loss of selectivity.

The composition of degraded AgF_2 is not known, but one component may very well be the lower-valent fluoride AgF. Not surprisingly, AgF is a much weaker fluorinating reagent than AgF_2. The ISKC reactions of C_{60} with pure AgF_2 and with pure AgF are compared in Fig. 2. The predominant fluorofullerene

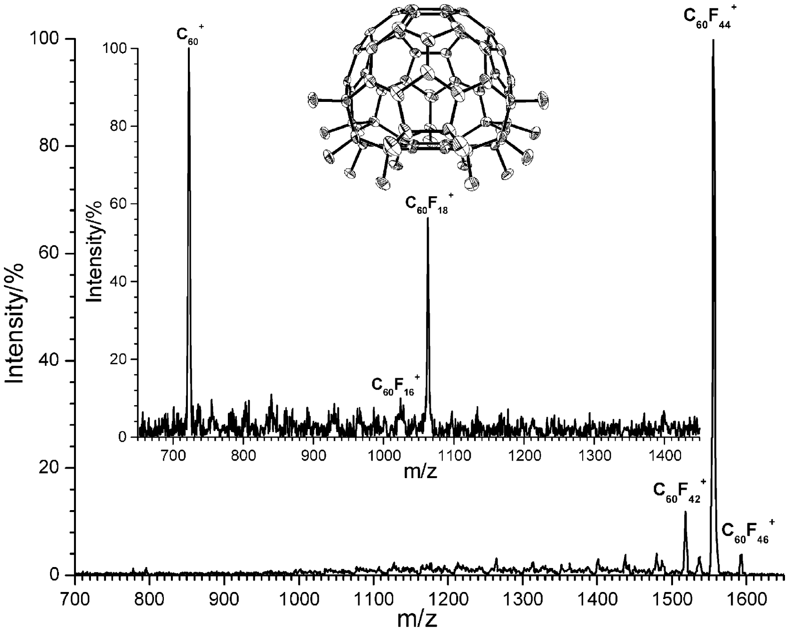

Fig. 2. EI mass spectrum from the ISKC fluorination of C_{60} with AgF_2 (300 °C, $U_e = 100$ eV, mass range 700–1650 Da). Inset: EI mass spectrum of the C_{60}/AgF reaction product (360 °C, $U_e = 70$ eV, mass range 650–1450 Da). Note the higher temperature for the AgF reaction: a mixture of C_{60} and AgF at 300 °C does not produce volatile highly fluorinated fullerenes. The X-ray structure of $C_{60}F_{18}$ from Ref. [20] is also shown.

products were $C_{60}F_{44}$ and $C_{60}F_{18}$, respectively. Even though the inset spectrum in Fig. 2 shows relatively pure $C_{60}F_{18}$, AgF cannot be used to selectively fluorinate C_{60} to $C_{60}F_{18}$ for two reasons. First, the isolated yields of $C_{60}F_{18}$ were much too small (note the presence of significant amounts of C_{60} in the inset spectrum). Second, gram-scale reactions resulted in the formation of a number of side products. One of these side products, $C_{60}(CF_3)_2$, was subsequently isolated and characterized [25].

Fluorinations of C_{60} with other binary metal fluoride including PbF_n [26] and CeF_n [22,27] were also studied by ISKC mass spectrometry, but these experiments will not be described in this paper.

3.2. Fluorinations of [60]fullerene with ternary metal fluorides other than K_2PtF_6

There were several reasons why we decided to study reactions of C_{60} with ternary metal fluorides such as K_2PtF_6, K_3CoF_6, and K_2NiF_6. First, ternary metal fluorides of this type are more numerous than the corresponding binary transition metal fluorides (consider K_2MnF_6 and Rb_2MnF_6 vs. MnF_4 and Cs_2PbF_6 and Cs_3PbF_7 vs. PbF_4). Second, these ternary compounds are generally weaker fluorinating reagents than the parent binary. This feature makes them easier to handle in the laboratory environment and, more importantly, opened up the possibility of isolating fluorofullerenes with a lower degree of fluorination.

3.2.1. K_3CoF_6

We recorded mass spectra of the volatile products of the ISKC reaction of C_{60} with K_3CoF_6 as a function of time at constant temperature. The gradual decrease in the degree of fluorination over time is shown in Fig. 3. At the beginning of the reaction, the main product was $C_{60}F_{36}$. Over time, however, the abundance of $C_{60}F_{36}$ decreased and that of $C_{60}F_{18}$ increased, and eventually the latter fluorofullerene was the main volatile product.

Furthermore, after 35 h of reaction, the intensity of the $C_{60}F_{18}{}^+$ ion current fell to zero, and only the C_{60}

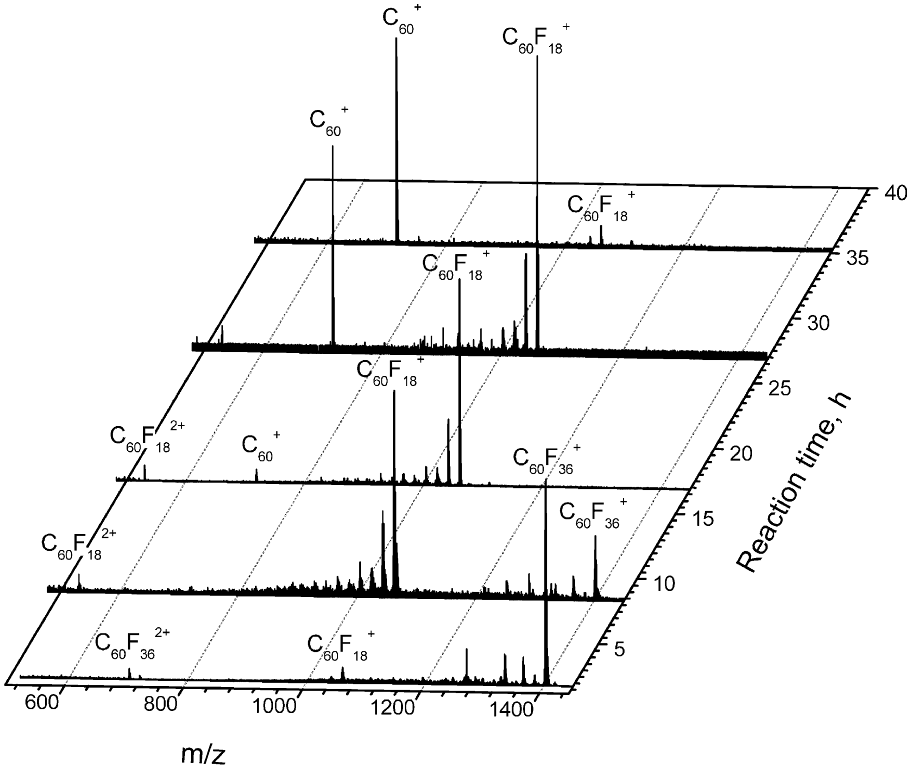

Fig. 3. Time-dependent EI mass spectra recorded during the ISKC fluorination of C_{60} with K_3CoF_6 (365 °C, $U_e = 70$ eV, mass range 500–1450 Da). Note the decrease in the degree of fullerene fluorination over time.

starting material was observed. Similar variations in product distributions over time were also observed using the ternary reagents K_2PtF_6 [22], Cs_3PbF_7 [26], $BaPbF_6$ [28], Na_3PbF_6 [28], and the physical admixture MnF_3/KF. In all cases a similar decrease in the degree of fluorination was observed and the main fluorofullerene at the end of the reaction was $C_{60}F_{18}$. A kinetic model for these reactions was proposed that satisfactorily explained many of the observed phenomena and predicted estimates of differences in the energies of activation for the sequential addition of fluorine atoms to the fullerene cage [28].

3.2.2. K_2NiF_6

This compound is a commercial reagent and is normally used as a convenient source of F_2, which is released upon heating. An ISKC reaction of C_{60} with a 60-fold molar excess of K_2NiF_6 was carried out from 230 to 330 °C. At the lower temperature, the main species observed were $C_{60}F_{48}^+$ (70%) and $C_{60}F_{46}^+$ (100%). At 330 °C, however, the intensity of $C_{60}F_{48}^+$ dropped and $C_{60}F_{46}^+$ became the dominant ion present. Note that compositionally pure $C_{60}F_{48}$ can be prepared from C_{60} and F_2 gas at 330 °C [9]. Thus, we see that K_2NiF_6, which had the highest fluorinating activity among the transition-metal fluorides we examined, was similar in fluorinating activity to F_2 and certain noble gas fluorides. However, unlike the direct fluorination of C_{60} with F_2 [9], the reaction of C_{60} with K_2NiF_6 did not result in the selective formation of $C_{60}F_{48}$.

3.2.3. KF/MnF_3

We had hoped that the addition of KF would reduce the fluorinating activity of MnF_3 and hence shift the level of fluorination of fullerene towards lower values.

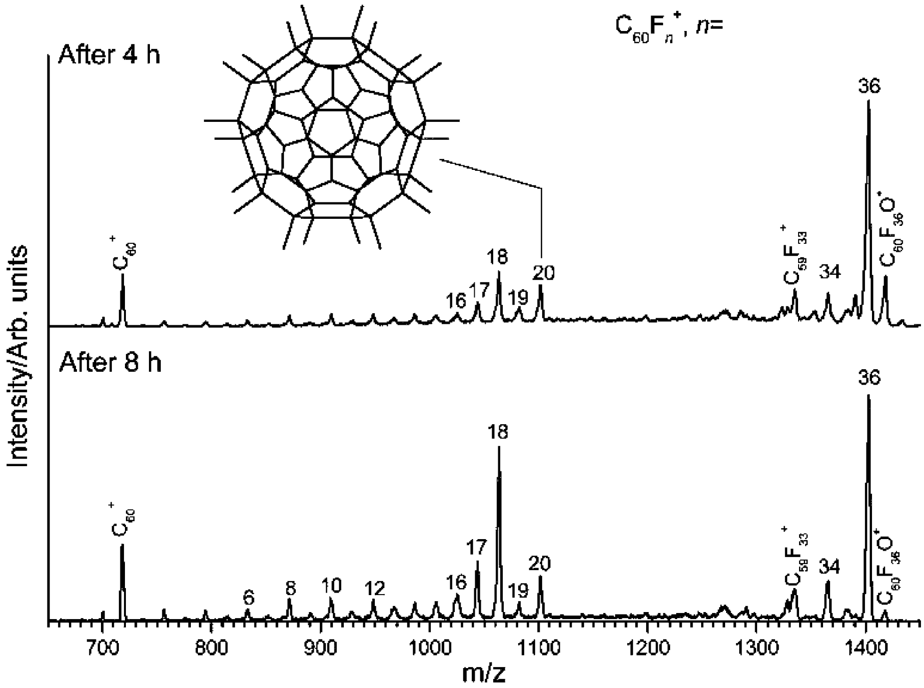

Fig. 4. EI mass spectra registered during the ISKC fluorination of C_{60} with MnF_3/KF (375 °C, $U_e = 70$ eV, mass range 650–1450 Da). Inset: proposed structure of $C_{60}F_{20}$.

Indeed, using a 1:1 KF/MnF_3 ratio, we observed $C_{60}F_{18}$ as the main product of the reaction with C_{60}, although with an undesirable decrease in the overall yield. Interestingly, under certain conditions we noticed a significant amount of a species with *m*/*z* 1100 (Fig. 4), which corresponds to the composition $C_{60}F_{20}$. By optimizing the reaction conditions, we were able to achieve a 10-fold increase in the yield of $C_{60}F_{20}$ in the product, which after HPLC purification allowed for the isolation of pure $C_{60}F_{20}$. According to its ^{19}F NMR spectrum, all twenty fluorine atoms in $C_{60}F_{20}$ are equivalent, suggesting that the molecule has five-fold symmetry with the fluorine atoms forming a ring-like array around the equator of the [60]fullerene cage [29]. The proposed D_{5d} structure, shown in the inset in Fig. 4, is reminiscent of the planet Saturn.

Related ISKC experiments in which elemental fluorine was used as the fluorinating reagent for a mixture of C_{60} and MnF_2 [30,31] have been reported. These reactions resulted in the sequential selective formation of $C_{60}F_{18}$ and $C_{60}F_{36}$. Note that the more highly fluorinated product was formed at a later stage of the reaction, in contrast to the solid-state metal-fluoride ISKC reactions described above.

3.3. Fluorinations of higher fullerenes and fullerene derivatives

In this section, we describe experiments with fullerene compounds other than C_{60}, some of which were only available to us in mg quantities. Our highly sensitive ISKC mass spectrometric experimental methodology was particularly valuable here because we could monitor the progress of fluorination reactions and detect the volatile reaction products even though we could not collect macroscopic samples for subsequent spectroscopic analysis.

3.3.1. Fluorination of C_{70}

The mass spectra recorded during the ISKC fluorination of C_{70} with MnF_3 contained predominantly $C_{70}F_{36}$, $C_{70}F_{38}$, and $C_{70}F_{40}$. The experiment performed in the evacuable glass reactor gave a similar distribution of products. This bulk product mixture was separated using HPLC into 49 fractions identified by ^{19}F NMR spectroscopy and mass spectrometry as $C_{70}F_{34}$ (one isomer), $C_{70}F_{36}$ (six isomers), $C_{70}F_{38}$ (eight isomers), $C_{70}F_{40}$ (at least five isomers), $C_{70}F_{42}$ (one isomer), $C_{70}F_{44}$ (one isomer), and some oxide and hydroxide derivatives [32]. We have not yet been successful in finding a more selective fluorinating reagent for [70]fullerene.

3.3.2. *Fluorination of C_{74}*

C_{74} belongs to the group of so-called small bandgap (SBG) fullerenes, which, unlike the common, commercially available fullerenes such as C_{60}, C_{70}, C_{76}, C_{78}, and C_{84}, possesses a very small energy gap between its highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively). To highlight the difference, compare the DFT-predicted bandgap of 0.05 eV for D_{3h} symmetry C_{74} with the HOMO–LUMO gap of 1.72 eV for C_{60} [11]. As another comparison, the electron affinity and ionization energy of C_{74}, are much higher and lower, respectively, than for similarly-sized fullerenes [4]. Such a large difference in electronic structure is responsible for the kinetic instability of SBG fullerenes such as C_{74} with respect to self-polymerization. It was reported that C_{74}, whose abundance in fullerene soot prior to extraction is comparable to that of C_{84}, is virtually absent in the fullerene extract [33]. Not surprisingly, there have been no attempts to study the chemical reactivity of [74]fullerene. The sample that we examined was contaminated with C_{60} and C_{70}. Nevertheless, mass spectrometry allowed us to identify all of the products, including the first observation of fluoro[74]fullerenes. The mass spectrum recorded during the reaction of C_{74} with MnF_3 at 410–510 °C is shown in Fig. 5. There are three main groups of ions, which correspond to fluorinated derivatives of C_{60}, C_{70}, and C_{74}. For a given value of n, $C_{60}F_n$ and $C_{70}F_n$ species are likely to be more volatile than higher-molecular weight $C_{74}F_n$ species. Therefore, the relative intensities of $C_{60}F_n^+$ and $C_{70}F_n^+$ ions may overestimate their actual abundance in the mixture of products. In any event, $C_{74}F_{38}$ is the predominant [74]fullerene molecular species formed in the

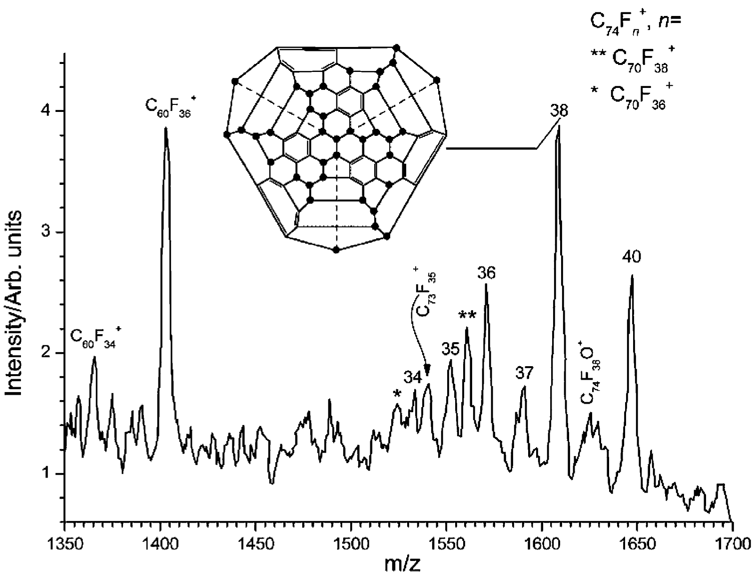

Fig. 5. EI mass spectrum recorded during in situ reaction of C_{74} with MnF_3 (450 °C, U_e = 150 eV, mass range 1350–1700 D). Inset: Schlegel-like diagram (• = F atom) looking down the C_3 axis for the proposed D_3 isomer of $C_{74}F_{38}$. The C_3 axis is formed by two carbon and two fluorine atoms, and one of each of these is hidden in this view.

fluorination of C_{74}. By analogy with the T-symmetry isomer of $C_{60}F_{36}$, which is believed to be especially stable because it possesses four isolated aromatic hexagons [23], we propose the D_3-symmetry structure for $C_{74}F_{38}$ represented by the Schlegel-like diagram in Fig. 5. This structure possesses six aromatic hexagons.

3.3.3. Fluorination of C_{76} and C_{84}

Products of the ISKC fluorination of C_{76} with MnF_3 (435–530 °C, Fig. 6) and K_2PtF_6 (410–470 °C, Fig. 7) were $C_{76}F_{38}$, $C_{76}F_{40}$ and $C_{76}F_{42}$ in the case of MnF_3, and $C_{76}F_{36}$ in the case of K_2PtF_6. In contrast to the reaction of C_{76} with MnF_3, drastic changes in the gas-phase product distribution was observed over time with K_2PtF_6. At the beginning ($T = 410\,°C$), the dominant ion was $C_{76}F_{36}^+$ (Fig. 7a). Raising the cell temperature to 430 °C caused the intensity of $C_{76}F_{36}^+$ to drop, and $C_{76}F_{34}^+$ became the dominant ion (Fig. 7b). Further heating resulted in a gradual decrease in the intensities of all ions except for $C_{76}F_{20}^+$, which at the final stage of the reaction had the highest intensity (Fig. 7c).

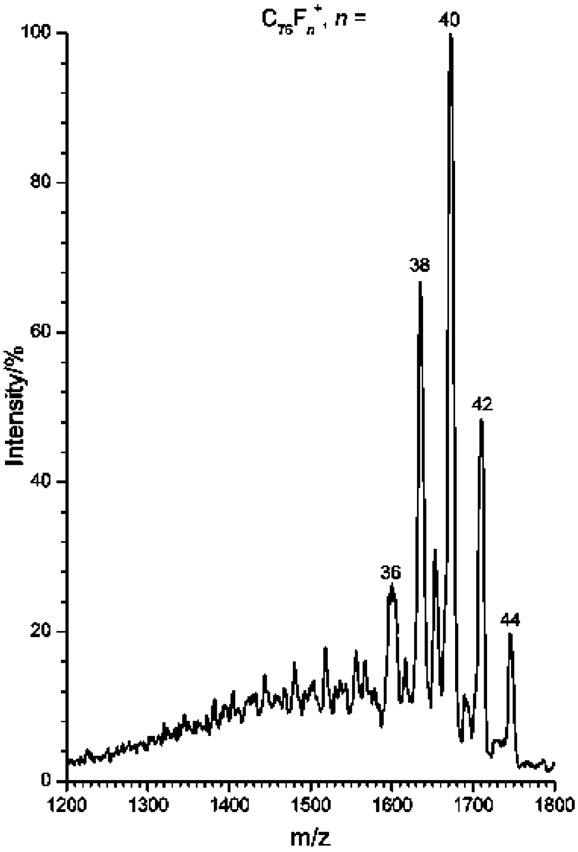

Fig. 6. EI mass spectrum recorded during the ISKC fluorination of C_{76} with MnF_3 (435 °C, $U_e = 70$ eV, mass range 1200–1800 Da).

Several interesting conclusions can be made from the analysis of the C_{76}/K_2PtF_6 mass spectra. First, fluorofullerene ions with an odd number of fluorine-atom substituents (e.g., $C_{76}F_{33}^+$ and $C_{76}F_{35}^+$) are almost certainly fragments of molecular species since they are electronically open shell species. Furthermore, the $C_{75}F_{33}^+$ ion is probably a fragment of the parent molecule $C_{76}F_{36}$ through loss of $CF_3^\bullet$ (recall that this was observed for $C_{60}F_{36}$). In some spectra, including Fig. 7b, the intensity of $C_{76}F_{35}^+$ was higher than that of the parent $C_{76}F_{36}^+$. We propose that such an unusual distribution of fluorofullerene ions originates from the presence of trifluoromethyl derivatives of fluoro[76]fullerenes and the specific fragmentation behavior of C–CF_3 bonds. It is known that $CF_3^\bullet$ loss is the main EI-fragmentation channel for $C_{60}F_n(CF_3)_m$ compounds, which are believed to form when $CF_3^\bullet$ radicals, which are generated by the thermal fragmentation of fluorofullerenes, are attached to remaining intact fullerene species (see also Section 3.4). In some cases, molecular ions even smaller than $(M–CF_3)^+$ fragments were observed [34]. Therefore, the high intensity of $C_{76}F_{35}^+$ most likely originates from the fragmentation of $C_{76}F_{35}CF_3$. Ions with an even number of substituents (e.g., $C_{76}F_{35}CF_3^+$, $C_{76}F_{36}^+$, $C_{76}F_{34}^+$, $C_{76}F_{25}CF_3^+$, and $C_{76}F_{20}^+$) can originate from either a molecular species or from a fragment. Our prior work has demonstrated that EI-fragmentation by loss of two consecutive fluorine atoms is not a likely process for fluorofullerenes. Moreover, the drastic change in relative intensities indicates that many of the observed species have different molecular precursors with, presumably, different volatilities (the volatility of a given fluorofullerene increases as the number of fluorine atom substituents increases). Not surprisingly, the intensities of fluorofullerenes with a greater number of fluorine atoms (e.g., $C_{76}F_{35}CF_3^+$, $C_{76}F_{36}^+$, $C_{76}F_{34}^+$,

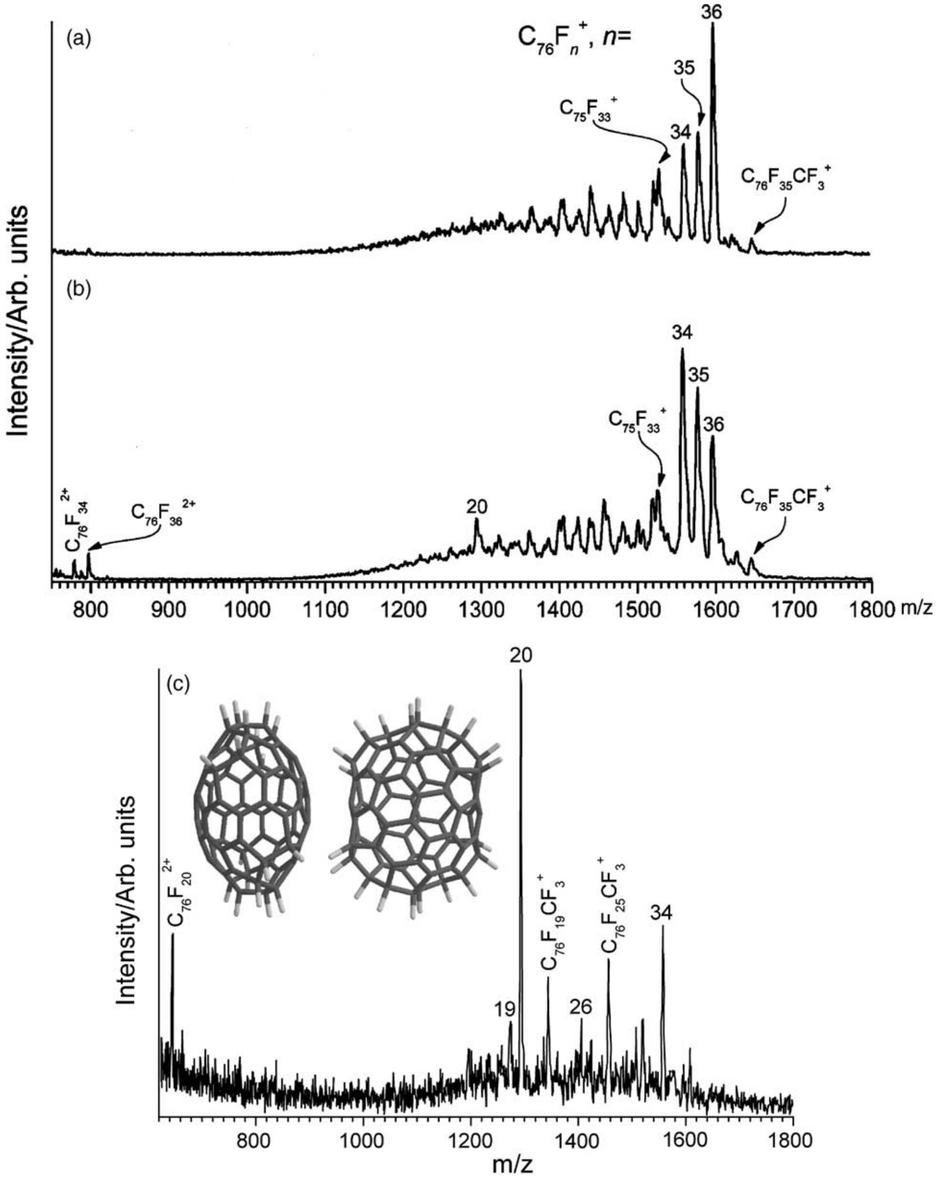

Fig. 7. EI mass spectra recorded during the ISKC fluorination of C_{76} with K_2PtF_6 ($U_e = 70$ eV): (a) $t = 0$ h, 410 °C, mass range 750–1800 Da; (b) $t = 1$ h, 430 °C, mass range 750–1800 Da; (c) $t = 3$ h, 430 °C, $U_e = 70$ eV, mass range 620–800 Da. Two views of the proposed structure of $C_{76}F_{20}$ are shown.

and $C_{76}F_{25}CF_3^+$), decreased over time, and $C_{76}F_{20}^+$ became the dominant peak (Fig. 7c).

Mass spectra from the ISKC fluorination of C_{84} with a 200-fold molar excess of CeF_4 at 450–500 °C and from two ISKC experiments with an 80-fold molar excess of K_2PtF_6 at 450–570 °C are shown in Fig. 8. Both reactions required higher temperatures than reactions of C_{60} for the same reagents. As a consequence, substantial amounts of a mono-CF_3 derivative of fluoro[84]fullerene, $C_{84}F_{39}CF_3$, were detected. The CeF_4 fluorination yielded one main product, $C_{84}F_{40}$, which was also a dominant species during the initial

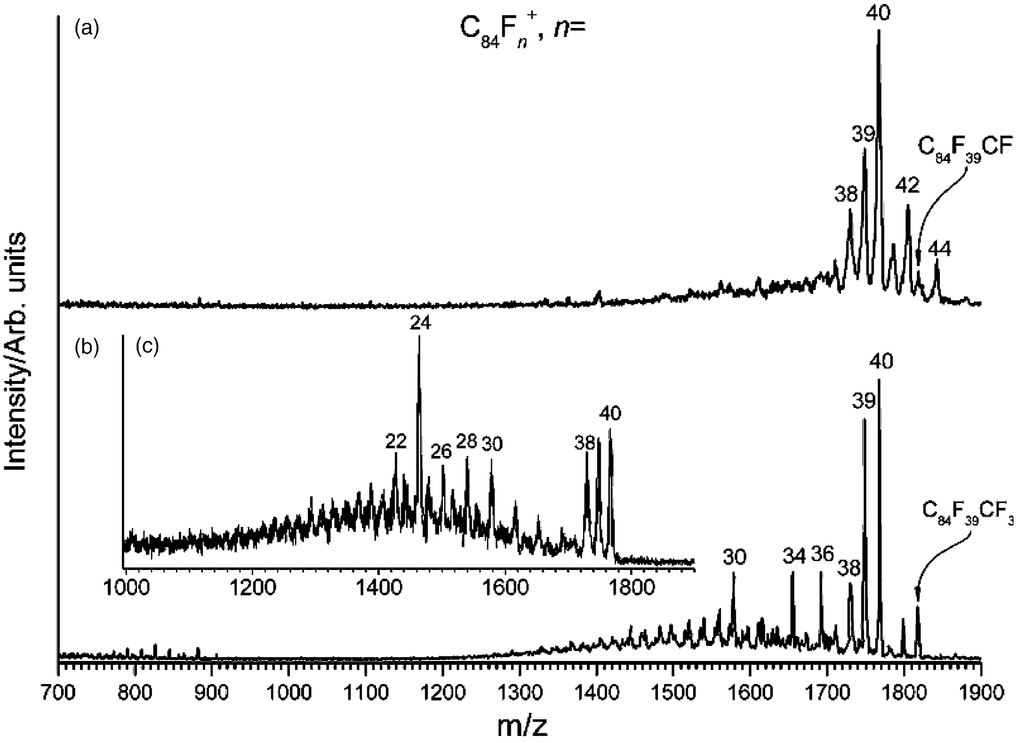

Fig. 8. EI mass spectra recorded during the ISKC fluorination of C_{84} with (a) CeF_4 (450 °C, $U_e = 70$ eV, mass range 700–1900 Da); (b) K_2PtF_6 (450 °C, $U_e = 100$ eV, mass range 700–1900 Da); and (c) K_2PtF_6 (570 °C, $U_e = 150$ eV, mass range 995–1900 Da).

stage of the K_2PtF_6 reaction. At a higher temperature, however, the K_2PtF_6 reaction produced species with fewer fluorine atoms, namely $C_{84}F_{36}{}^+$, $C_{84}F_{34}{}^+$, and $C_{84}F_{30}{}^+$ (Fig. 8b). Furthermore, when the temperature was raised to 570 °C, $C_{84}F_{24}{}^+$ became the most intense ion in the spectrum (Fig. 8c). This behavior is reminiscent of the ISKC fluorination of C_{60} with excess K_2PtF_6 or K_3CoF_6, where the dominant ion was initially $C_{60}F_{36}{}^+$ but was replaced by the less volatile $C_{60}F_{18}{}^+$ over time (by less volatile we mean that the neutral compound $C_{60}F_{18}$ is less volatile than the neutral compound $C_{60}F_{36}$).

The amounts of higher fullerenes available to us were too small to perform macroscopic syntheses in the evacuable glass apparatus. However, the amounts of products collected from the MnF_3 ISKC reaction were sufficient for HPLC purification, and as a result $C_{76}F_{38}$ (one isomer), $C_{76}F_{40}$ (five isomers) and $C_{84}F_{40}$ (at least two isomers) were isolated and partially characterized spectroscopically [10]. Further work will be needed for the complete characterization of these derivatives. In particular, the new fluorofullerenes $C_{76}F_{20}$ and $C_{84}F_{24}$ deserve attention as they may have highly symmetric structures and may have relatively high thermal stability.

The efficiency and reliability of quantum chemical calculations on polyatomic molecules has significantly improved in recent years, to the point where predictions of the most likely (i.e., the most stable) structures for newly observed derivatives can be made even before they have been isolated and spectroscopically characterized.

The AM1-predicted addition patterns in C_{76} hydrides, including $C_{76}H_{20}$, have been reported [35]. Similar computational studies of C_{60} hydrides and fluorides [36,37] have demonstrated a strong correlation between the relative stabilities of hydro- and fluorofullerene molecules with similar addition patterns.

Since this correlation is probably due to the universal character of carbon cage distortions upon the transition of carbon atoms from sp^2 to sp^3 hybridization, one might expect analogous behavior for C_{76} derivatives. As was previously noted [35], the curvature of the C_{76} cage is far from uniform; therefore, the addition of fluorine atoms to the most highly curved regions of the [76]fullerene cage is expected to produce the most stable derivatives. Two major types of structures were analyzed for $C_{76}H_{20}$ [35]: those incorporating a T-type addition, crown-like region as in $C_{60}F_{18}$ [20]; and those incorporating S-type fluorine-atom additions such as those proposed for the lower fluorides of C_{60} [38] and in $C_{60}F_{20}$ [29].

We examined computationally the relative stabilities of various $C_{76}F_{20}$ isomers. Full optimization of the geometry of all 11,628 isomers of with D_2 symmetry, as well as of a number of less symmetric isomers with belt- and crown-like fluorine atom arrangements, was carried out at the AM1 level of theory. The crown-like isomers included those with isolated benzenoid, naphthalenoid, and larger aromatic subunits on the carbon cage. At the second stage, several of the AM1-predicted most stable isomers were reexamined with full geometry optimization at the DFT level of theory [39]. As a result, two isomers of $C_{76}F_{20}$ were found to be at least 150 kJ/mol more stable than all the others. The more stable of the two isomers (by 15 kJ/mol) is shown in Fig. 7c. It was found to have D_2 symmetry and contained two 10-fluorine-atom regions of S-type additions (reminiscent of the 20-fluorine atom belt predicted for $C_{60}F_{20}$). It has the same addition pattern as that predicted for the most stable isomer of $C_{76}H_{20}$ [35]. The other stable isomer has C_2 symmetry and is also based on an S-type addition pattern. Since $C_{76}F_{20}$ is formed selectively, one might expect its structure to reveal a certain completeness (i.e., completeness in the sense that the structures of $C_{60}F_{18}$ and $C_{60}F_{20}$ represent a completely fluorinated region or belt, respectively). The two separated fluorine-atom S-type addition regions in the most stable D_2 isomer of $C_{76}F_{20}$ cannot be interconnected or even extended by additional S-type additions without encountering severe steric strain. Therefore, the predicted D_2 structure represents a kinetic “dead-end”, and nicely accounts for the observed compositional selectivity in the fluorination of C_{76}.

3.3.4. Fluorination of $(C_{59}N)_2$

We performed ISKC fluorinations of bis(aza[60] fullerene) $(C_{59}N)_2$, with MnF_3 at 300–450 °C and with K_2PtF_6 at 410–450 °C. The results of the MnF_3 fluorination are illustrated by Fig. 9. The most stable $C_{59}NF_n{}^+$ ions are expected to be closed shell species with odd n values, and these are the most abundant ions in the spectrum. The $C_{59}NF_{33}{}^+$ ion has the greatest intensity and the $C_{59}NF_{37}{}^+$ ion has the greatest number of fluorine atoms. In the K_2PtF_6 reaction, $C_{59}NF_{31}{}^+$ and $C_{59}NF_{33}{}^+$ were the main ions, with a significant abundance of $C_{59}NF_{19}{}^+$. Purification of the isolated product mixture by HPLC and characterization by ^{19}F NMR spectroscopy and EI mass spectrometry showed that the new fluoroazafullerenes. $C_{59}NF$, $C_{59}NF_5$, $C_{59}NF_{17}$, and $C_{59}NF_{33}$ had been prepared [40]. Various trifluoromethyl derivatives, especially those of $C_{59}NF_5$ (e.g., $C_{59}NF_4CF_3$, $C_{59}NF_3(CF_3)_2$ and $C_{59}NF_2(CF_3)_3$), were also isolated. Their presence is presumably due to the greater propensity to $CF_3{}^\bullet$ formation (i.e., the lower stability) of the fluorinated heterofullerene cage relative to fluorinated all-carbon fullerene cages. The formation of $C_{59}N$ derivatives with specific numbers of fluorine atoms and/or trifluoromethyl groups (e.g., 5, 17, and 33) can be rationalized in terms of their increased aromaticity relative to $(C_{59}N)_2$ [40]. The Schlegel diagram for the proposed structure of $C_{59}NF_{33}$ is shown in Fig. 9.

3.4. Trifluoromethylation of C_{60}

As previously mentioned, the addition of an adventitious CF_3 or C_2F_5 group can occur during ISKC fluorination reactions. $C_{60}F_{17}CF_3$ was isolated from the K_2PtF_6 reaction mixture and the structure of its main isomer, shown in Fig. 10, was determined by single-crystal X-ray diffraction [41]. The structure proved unambiguously that a CF_3 group was directly attached to the fullerene cage *of an isolable compound* and that, in this particular isomer, it occupied one of

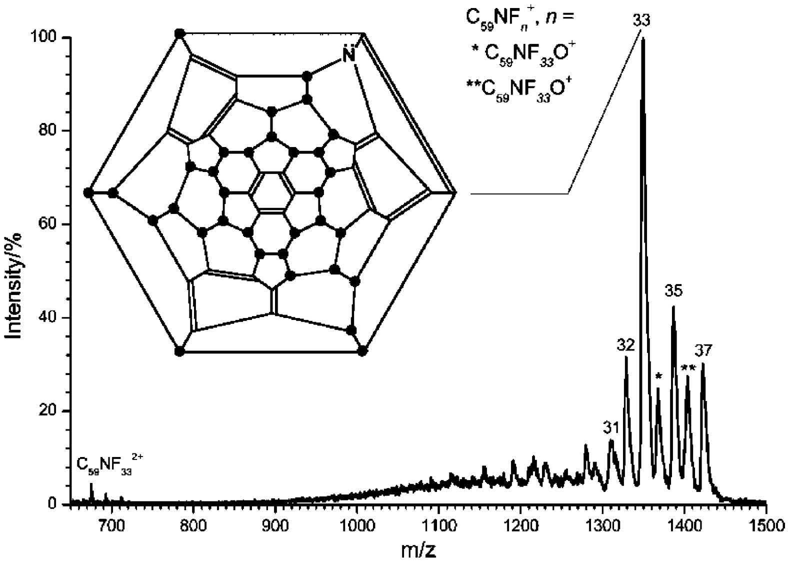

Fig. 9. EI mass spectrum recorded during the ISKC fluorination of $(C_{59}N)_2$ with MnF_3 (450 °C, $U_e = 70$ eV, mass range 650–1500 Da). Inset: Schlegel diagram of the proposed structure of $C_{59}NF_{33}$.

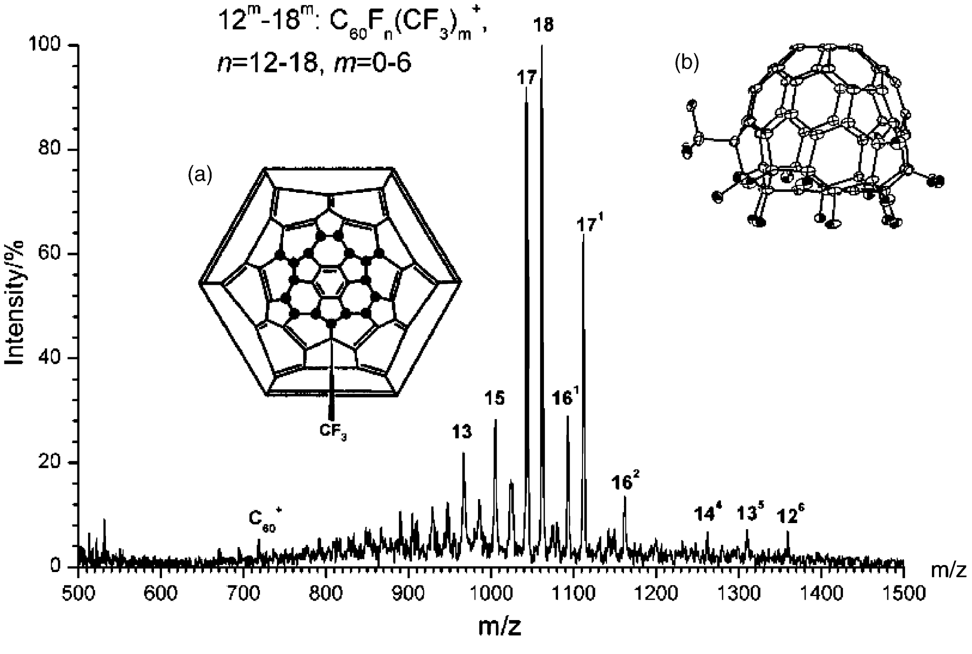

Fig. 10. EI mass spectrum recorded during the ISKC reaction of C_{60} with a K_2PtF_6/AgTFA mixture (375 °C, $U_e = 140$ eV, mass range 500–1500 DA). Insets: Schlegel diagram (a) and drawing of the structure for $C_{60}F_{17}CF_3$ (main isomer) (b).

the three positions of the sterically least demanding fluorine atoms in the structure of $C_{60}F_{18}$.

How many CF_3 groups can be added to [60]fullerene? For a given value of n, would the structure and properties of $C_{60}(CF_3)_n$ be the same, or even similar, to the structure and properties of $C_{60}F_n$? Would fullerenes having a mixture of fluorine atoms and CF_3 groups have useful, even practical, properties? With these questions in mind, we designed two series of ISKC experiments to intentionally add trifluoromethyl groups to C_{60}. In the first series of experiments, AgTFA, a source of CF_3 radicals when thermally decomposed, was added to the C_{60}/K_2PtF_6 reaction mixture. Mass spectra for this reaction at 375 °C and at 430 °C are shown in Figs. 10 and 11, respectively. At both temperatures, a series of $C_{60}F_n(CF_3)_m{}^+$ ions was observed. Ions with even $n+m$ values are molecular species, while ions with odd $n+m$ are almost certainly fragments. During the initial stage of each reaction, $C_{60}F_{17}CF_3{}^+$ and $C_{60}F_{18}{}^+$ were the dominant molecular ions. The abundant $C_{60}F_{17}{}^+$ ion in Fig. 11 is not usually observed in EI mass spectra of pure samples of $C_{60}F_{18}$, and therefore represents the $(M–CF_3)^+$ fragmentation product of $C_{60}F_{17}CF_3$.

Significantly, the addition of AgTFA as a trifluoromethylating reagent produced, for the first time, fluorofullerenes with more than one CF_3 group, including the molecular species $C_{60}F_{16}(CF_3)_2{}^+$ and $C_{60}F_{15}(CF_3)_3{}^+$. Fragment ions such as $C_{60}F_{16}CF_3{}^+$ and $C_{60}F_{15}(CF_3)_2{}^+$, which result from CF_3 loss, and $C_{60}F_{15}(CF_3)_2{}^+$, which results from loss of a fluorine atom, respectively, were also observed.

By analogy with the structure of the (more abundant [41]) isomer of $C_{60}F_{17}CF_3$ shown in Fig. 10, we propose that the most likely isomers of $C_{60}F_{16}(CF_3)_2$ and $C_{60}F_{15}(CF_3)_3$ are those in which the trifluoromethyl groups occupy two or three positions, respectively, of the three sterically least demanding fluorine atoms in $C_{60}F_{18}$. The proposed isomer of $C_{60}F_{15}(CF_3)_3$ in shown in Fig. 11.

During the initial stage of the 430 °C K_2PtF_6/AgTFA experiment, we detected a group of previously-unknown ions with the formulas $C_{60}F_{20-n}(CF_3)_n{}^+$ (n = 1–6). At a later stage of the reaction, but at the

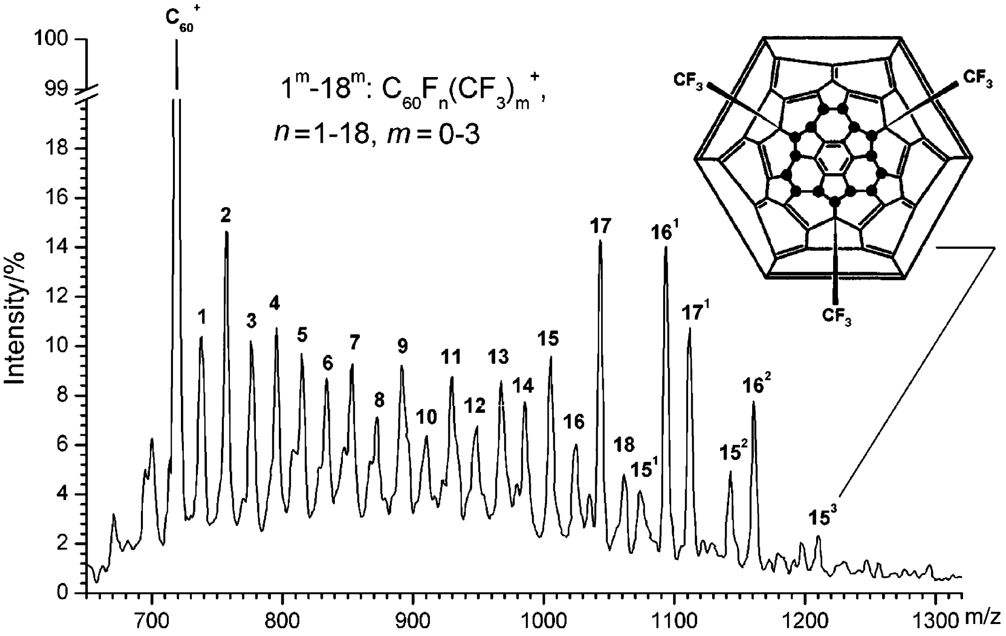

Fig. 11. EI mass spectrum recorded during the ISKC reaction of C_{60} with K_2PtF_6/AgTFA (430 °C, U_e = 70 eV, mass range 650–1320 Da). Inset: Schlegel diagram (• = F atom) for the proposed structure of $C_{60}F_{15}(CF_3)_3$.

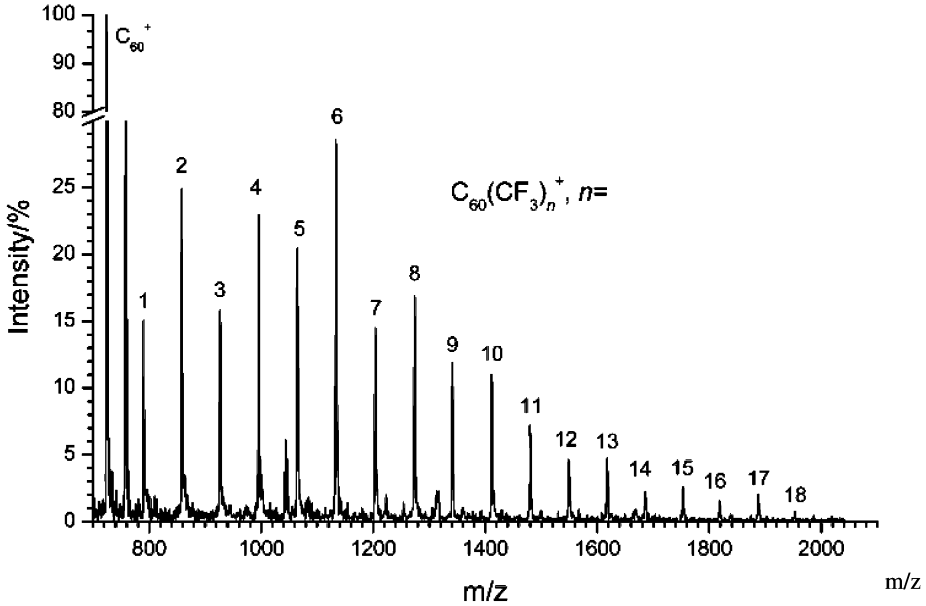

Fig. 12. EI mass spectrum recorded during the ISKC reaction of C_{60} with AgTFA (300 °C, $U_e = 100$ eV, mass range 700–2100 Da).

same temperature, we observed another group of ions, $C_{60}F_{18-n}(CF_3)_n^+$ ($n = 2$–5), which also had not been observed before (Fig. 11). In addition, the products included significant amounts of fluorofullerenes with relatively few fluorine atoms, such as $C_{60}F_{2n}^+$ ($n = 1$–4) and $C_{60}F_mCF_3^+$ ($m = 1, 3$). However, the selectivity would need to be greatly improved before this could be considered for a practical synthesis of new fluorofullerenes, with or without CF_3 groups.

In the second series of experiments, we performed an ISKC "direct trifluoromethylation" of C_{60} with a 60-fold molar excess of AgTFA. The mass spectrum in Fig. 12 shows that $C_{60}(CF_3)_n^+$ ions with $n = 1$–18 were observed at temperatures as low as 210 °C. The significance of this is two-fold. First, as expected, the volatilities of trifluoromethylated [60]fullerenes are higher than those of fluorofullerenes with the same number of substituents. More importantly, the formation of $C_{60}(CF_3)_n$ compounds occurred under much milder conditions than are typically required for the fluorination of fullerenes with metal fluorides.

Appearance energy (AE) measurements demonstrated that ions with odd values of n, and C_{60}^+, are fragments, while species with even values of n are most likely molecular ions (the differences in AE values for the two groups were 3–4 eV). Significantly, $C_{60}(CF_3)_n^+$ ions with odd values of n in the high mass region ($n = 11$–18) were more abundant than the ions with even values of n (e.g., note that the intensity of $C_{60}(CF_3)_{17}^+$ is higher than the intensity of either $C_{60}(CF_3)_{18}^+$ or $C_{60}(CF_3)_{16}^+$). However, ions with even n are more abundant than those with odd n in the low mass region ($n = 1$–8). The reasons why the high-mass species appear to be more prone to fragmentation, and why that fragmentation occurred almost exclusively by the loss of intact CF_3 groups and not by other channels, are not yet understood.

4. Conclusions

Nearly a decade of experimental work from our lab using the in situ Knudsen-cell (ISKC) technique has proven that it has distinct advantages over traditional methods of exploratory synthesis. It allowed for the rapid screening of different sets of reaction

Table 1
Fullerene fluorination products from ISKC syntheses[a]

Fullerene substrate	Fluorinating reagent	Temperature range (°C)	Predominant product(s) in ISKC experiment	Subsequent isolated products[b]	Reference
C_{60}	AgF	360–450	$C_{60}F_{18}$, $C_{60}(CF_3)_2$	$C_{60}(CF_3)_2$	[25]
	AgF_2	300	$C_{60}F_{44}$		
	MnF_3	300–500	$C_{60}F_{36}$	$C_{60}F_{36}$ (C_3, T)	[23]
				$C_{60}F_{36}$ (C_1)	[42]
	KF/MnF_3	375	$C_{60}F_{36}$, $C_{60}F_{20}$, $C_{60}F_{18}$	$C_{60}F_{20}$ (D_{5d})	[29]
	K_2PtF_6	320–500	$C_{60}F_{36}$, $C_{60}F_{18}$	$C_{60}F_x$ ($x = 2$–8)	[43]
				$C_{60}F_xO$ ($x = 2$–8)	[44]
				$C_{60}F_{16}$ (C_s)	[45]
				$C_{60}F_{18}$ (C_{3v})	[19]
				$C_{60}F_{18}O$	[46,47]
				$C_{60}F_{18}O_2$	[48]
				$C_{60}F_{17}CF_3$	[41]
	K_3CoF_6	365	$C_{60}F_{36}$, $C_{60}F_{18}$		
	K_2NiF_6	230–330	$C_{60}F_{48}$, $C_{60}F_{46}$		
C_{70}	MnF_3	410–510	$C_{70}F_{36}$, $C_{70}F_{38}$, $C_{70}F_{40}$	$C_{70}F_{34}$, $C_{70}F_{36}$, $C_{70}F_{38}$, $C_{70}F_{40}$, $C_{70}F_{42}$, $C_{70}F_{44}$	[32]
C_{74}	MnF_3	410–510	$C_{74}F_{38}$		
C_{76}	MnF_3	435–530	$C_{76}F_{38}$, $C_{76}F_{40}$, $C_{76}F_{42}$	$C_{76}F_{36}$, $C_{76}F_{38}$, $C_{76}F_{40}$ $C_{76}F_{42}$ $C_{76}F_{44}$, $C_{76}F_{40}O$	[10,49]
	K_2PtF_6	410–470	$C_{76}F_{36}$, $C_{76}F_{34}$, $C_{76}F_{20}$		
C_{84}	CeF_4	450–500	$C_{84}F_{40}$	$C_{84}F_{40}$, $C_{84}F_{44}$	[10]
	K_2PtF_6	450–570	$C_{84}F_{40}$, $C_{84}F_{36}$, $C_{84}F_{34}$, $C_{84}F_{30}$, $C_{84}F_{24}$		
$(C_{59}N)_2$	MnF_3	300–450	$C_{59}NF_{37}$, $C_{59}NF_{33}$		
	K_2PtF_6	410–450	$C_{59}NF_{33}$, $C_{59}NF_{31}$, $C_{59}NF_{19}$	$C_{59}NF_{33}$, $C_{59}NF_{17}$, $C_{59}NF_5$, $C_{59}NF$, $C_{59}NF_x(CF_3)_y$ ($x = 2, 3, 4$, $y = 1, 2, 3$)	[40]

[a] All ISKC data are from this work.

[b] These compounds were isolated from bulk syntheses based on the ISKC results. Their synthesis, purification, and characterization were reported in the indicated references. The point group symmetry of some of the products is shown in parentheses.

conditions in one experiment, with simultaneous identification of the products in real time. The ISKC technique allowed us to efficiently optimize yields of selectively fluorinated derivatives of C_{60} and C_{70}. This information was then used to successfully design synthetic procedures for preparing macroscopic amounts of specific products as summarized in Table 1 [42–49].

As a result of our ISKC studies of C_{60}/MnF_3, C_{60}/CeF_4 and C_{60}/K_2PtF_6, for example, we were able to produce hundreds of milligrams of the 90+%-compositionally-pure fluorofullerenes $C_{60}F_{36}$ and $C_{60}F_{18}$. (In the case of $C_{60}F_{18}$, single crystals were obtained, obviating the need for tedious HPLC separations [50].) In favorable cases, small amounts of ISKC reaction products could be collected directly from the mass spectrometer on a cold plate for additional spectroscopic characterization, even before macroscopic amounts were available.

The fullerene C_{60}, with its remarkable stability and high symmetry and with 30 double bonds available for addition reactions, was found to be a unique and convenient substrate for studying a wide range of reagents [13]. Because of this, an additional result of this work was the development of a self-consistent scale of relative reactivities for a wide variety of fluorinating agents, based on the number of fluorine atoms in the $C_{60}F_n$ products. An equally useful but different scale of the fluorinating activity has been reported by Christe and Dixon [51]. Unfortunately, there is no overlap between our set of fluorinating agents and theirs at the present time, so a comparison of the two scales is not yet possible.

An additional advantage of the ISKC technique is that many exploratory reactions can be carried out on fullerenes that are very expensive and/or are only available in mg or sub-mg quantities, such as higher fullerenes, endohedral metallofullerenes, and heterofullerenes. Since the products must be volatilized from the Knudsen cell and therefore must be thermally stable, this provides information on the specific compositions of the most stable new derivatives even if macroscopic amounts of these new derivatives have not yet been isolated.

Finally, it should be realized that the ISKC technique could be applied (i) to reagents other than fluorinating reagents and (ii) to substrates other than fullerenes provided that the products are thermally stable and sufficiently volatile to be detected by mass spectrometry. An example of the former is the trifluoromethylation of C_{60} discussed in Section 3.4. An example of the latter, in which a volatile fluorinating reagent was used, can be found in references [30,31].

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