A mass spectrometric study of $C_{60}F_{48}$

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The first observation of the EI mass spectrum of the $C_{60}F_{48}$ molecule and results on the study of the evaporation behaviour of $C_{60}F_{48}$ samples by Knudsen cell mass spectrometry are reported.

Fluorinated fullerenes can be easily obtained by fluorination with fluorine gas,[1–6] and a wide range of fluorinated products $C_{60}F_{2n}$ ($2n = 36$–48) has been reported. Due to the thermal stability of fluorofullerenes mass spectrometry represents a most convenient tool for the identification and composition characterisation in the gas phase. However, in some mass spectrometry techniques the ionisation of fluorinated fullerenes is accompanied by strong fragmentation/decomposition (laser desorption, LD),[1] ion/molecule reactions resulting in coalescence products (FAB),[2] which adds complexity in the interpretation of the mass spectra.

A detailed comparative analysis of the mass spectra obtained using various mass spectrometry methods such as LD, electron impact (EI), electron capture (EC) and field desorption (FD) has been performed by Tuinman *et al.*[1] Using the above techniques for the analysis of the same fluorofullerene sample $C_{60}F_{44–46}$, they found that the relative abundance of fluorinated species in the mass spectrum depends to a significant extent on the method of ionisation/desorption. The $C_{60}F_{44}^+/C_{60}F_{46}^+$ ratio was higher in the mass spectra of thermal desorption (TD) (which precedes EI and EC ionisation) and LD in comparison with FD mass spectrum. FD was nevertheless found to 'be milder than EI, not only in the amount of internal energy imparted by the ionisation itself but also in the degree of heating required before ions are observed'.[1] Therefore, the difference in the mass spectra is dictated by some loss of F_2 from $C_{60}F_{46}$ during TD. In the report on the synthesis of $C_{60}F_{48}$ the same ionisation techniques were used: EI, EC and FD.[3] It was reported that the highest relative intensity of the $C_{60}F_{48}^+$ signal in the FD mass spectrum comprised 69% of the total intensity of $C_{60}F_{2n}^+$ ($2n = 40$–48) ions, while EI and EC gave a lower relative abundance of $C_{60}F_{48}^+$ (not given in the paper). No other complementary methods were applied for the quantitative characterisation of the $C_{60}F_{48}$ samples, thus preventing estimations of their purity. Thus, it has remained unclear whether mass spectrometry techniques could be applied for the composition characterisation of the fluorofullerenes.

In the present work we apply the method of Knudsen cell mass spectrometry (KCMS) for the study of evaporation behaviour of $C_{60}F_{48}$ samples and report the first observation of the EI mass spectrum of $C_{60}F_{48}$.

$C_{60}F_{48}$ samples have been produced in reaction of pure C_{60} (99.8%, TERM USA) with fluorine gas by the method similar to that described elsewhere.[4] Sample 1 was prepared by fluorination for 12 h ($T_{\max} = 350$ °C), and sample 2 for 6 h ($T_{\max} = 315$ °C). The composition of both samples according to chemical elemental analysis corresponds to $C:F = 60:48\pm1$. However, we note here that this method does not allow one to distinguish between 100% pure $C_{60}F_{48}$ and a sample consisting of 50% $C_{60}F_{46}$ and 50% $C_{60}F_{48}$. EI mass spectra were obtained using a magnetic sector mass spectrometer MI-1201 (Russia) combined with a high temperature ion source operated under EI conditions (70 eV). The weighed amount (18.1 and 15.4 mg, respectively) of fluorinated fullerene sample was placed into a nickel effusion cell. The cell was resistively heated to 433–558 K and temperature was measured with a Pt/Pt–Rh thermocouple.

The EI mass spectra of samples 1 and 2 are shown in Figures 1 and 2, respectively. The major peak at 1632 *m/z* in the spectrum of sample 1 corresponds to $C_{60}F_{48}^+$. Relative intensities of fragment ions comprise 17% of the molecular ion. The observed fragment ions were assigned as follows. A group of ions $C_{60-n}F_{48-3n}^+$: $C_{59}F_{45}^+$ (17%), $C_{58}F_{42}^+$ (5%), $C_{57}F_{39}^+$ (5%) differs by *m/z* 69 which corresponds to $CF_3^{\cdot}$ loss. Ions $C_{60}F_{47}^+$ (13%), $C_{58}F_{43}^+$ (7%), $C_{57}F_{41}^+$ (11%), $C_{56}F_{39}^+$ (4%) arise from the loss of radicals $F^{\cdot}$, $C_2F_5^{\cdot}$, $C_3F_7^{\cdot}$ and $C_4F_9^{\cdot}$, respectively; and ions $C_{59}F_{46}^+$ (13%), $C_{59}F_{44}^+$ (12%) are formed due to the loss of fragments CF_2 and CF_4. Thus, one may

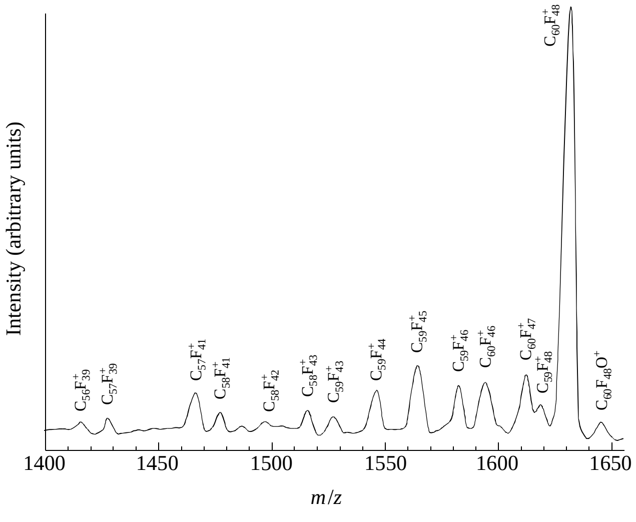

Figure 1 EI mass spectrum of sample 1 at $T = 558$ K in the mass range 1400–1690 amu.

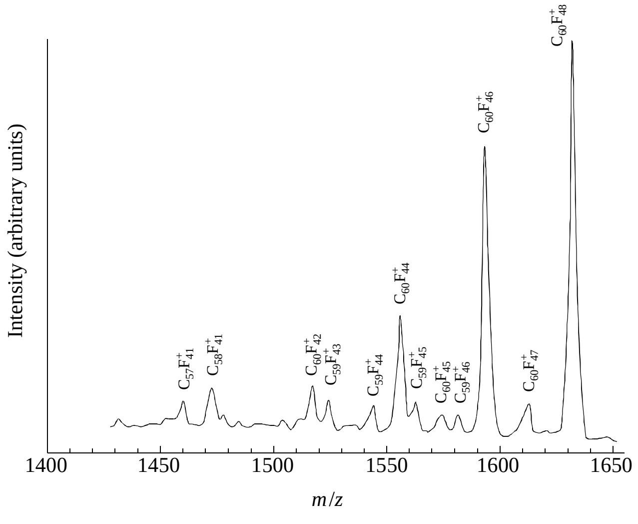

Figure 2 EI mass spectrum of sample 2 at $T = 535$ K in the mass range 1400–1690 amu.

conclude that the mass spectrum in Figure 1 represents the mass spectrum of a single molecule $C_{60}F_{48}$. The origin of the $C_{59}F_{48}^+$ peak (8%) is not certain: it could either come from detachment of the C radical from the molecule $C_{60}F_{48}$ (which has not been observed earlier for fluorinated fullerenes) or it could originate from the oxofluoride $C_{60}F_{48}O$ as a result of detachment of the CO group. The relatively low abundance of oxides in the $C_{60}F_{48}$ samples does not allow assignment of the observed intensity of $C_{59}F_{48}^+$ to a fragment of oxygenated fluorofullerene species, however. It is very unlikely that this ion could arise as a product of fragmentation of higher fluorides $C_{60}F_{n>48}$, since no corresponding molecular ions were observed in the mass spectra.

We performed further experiments in order to determine possible precursors of the $C_{60}F_{46}^+$ ion in the EI mass spectrum. Mass spectra were recorded using an apparatus AutospecQ (Fisons, VG-Analytical) of $EBEQ_1Q_2$ configuration which allows a variation in energy of the ionising electrons (U_e) over a wide range. On decreasing U_e from 70 to 10 eV we found the $C_{60}F_{48}^+/C_{60}F_{46}^+$ ratio to be constant, whereas the signal $C_{60}F_{47}^+$ disappeared. Evidently, $C_{60}F_{46}^+$ is a molecular ion, but not a fragmentation product. Therefore, the most abundant peaks $C_{60}F_{2n}^+$ in the mass spectra of fluorofullerenes originate from the corresponding molecular species.

Indirect evidence in favour of the above conclusion was obtained from the collision induced dissociation (CID) mass spectrum of parent ion $C_{60}F_{48}^+$ presented in Figure 3. This shows that as a result of CID, $C_{60}F_{46}^+$ ions are not produced, while all the other fragment species are present in both CID and EI spectra (*cf.* Figure 1). Thus, the approximate contribution of fragment ions $C_{60}F_{46}^+$ and $C_{60}F_{44}^+$ can be estimated as < 5% of the intensity of $C_{60}F_{48}^+$, if at all, and the EI mass spectrum (E = 70 eV) of sample 1 (Figure 1) can be ascribed to a single molecule $C_{60}F_{48}$, with $C_{60}F_{46}$ being a minor (< 10%) impurity in the $C_{60}F_{48}$ sample prepared in this way.

Knowledge of the EI mass spectrum of $C_{60}F_{48}$ helped us to study in detail the evaporation behaviour of fluorofullerenes. The mass spectrum of sample 1 was recorded at 433 K as a function of time. At first the ions $C_{60}F_{42}^+$ and $C_{60}F_{44}^+$ dominated the spectrum [Figure 4(*a*)]. After 3 h the character of ion distribution drastically changed in comparison with the initial mass spectrum: the $C_{60}F_{48}^+$ ion became the most intense peak whereas intensities of the ions $C_{60}F_{2n<48}$ diminished by a factor of 5 [Figure 4(*c*)]. On raising the temperature to 558 K lower mass molecular ions (except $C_{60}F_{46}^+$) disappeared while $C_{60}F_{48}^+$ remained the major peak in the mass spectrum. No thermal degradation of $C_{60}F_{48}$ with F_2 loss was observed. It is noteworthy that this change in the mass spectrum occurred irreversibly, *i.e.* further decrease of the temperature did not reproduce the initial spectrum. Apparently, the presence of $C_{60}F_{46}^+$ in a constant 1:10 proportion to $C_{60}F_{48}^+$ indicates the true content of $C_{60}F_{46}$ molecules in the prepared sample 1. Consequently, the composition of sample 2 can be characterised as a mixture of $C_{60}F_{48}$, $C_{60}F_{46}$, $C_{60}F_{44}$ and $C_{60}F_{42}$ in the 10:7:3:1 ratio, respectively. The presence of small amounts of fluorides $C_{60}F_{x<48}$ in the sample 1 as an indication of incomplete fluorination could be the simplest explanation of the observed effect, though this might seem to contradict the common view that fluorides of very similar size and physical properties are likely to form a solid solution when they are mixed together. Evidently they would have very similar volatilities. Thus, one would expect much lower intensities of the minor components $C_{60}F_{46}$ and $C_{60}F_{44}$ with respect to $C_{60}F_{48}$ than was observed experimentally.

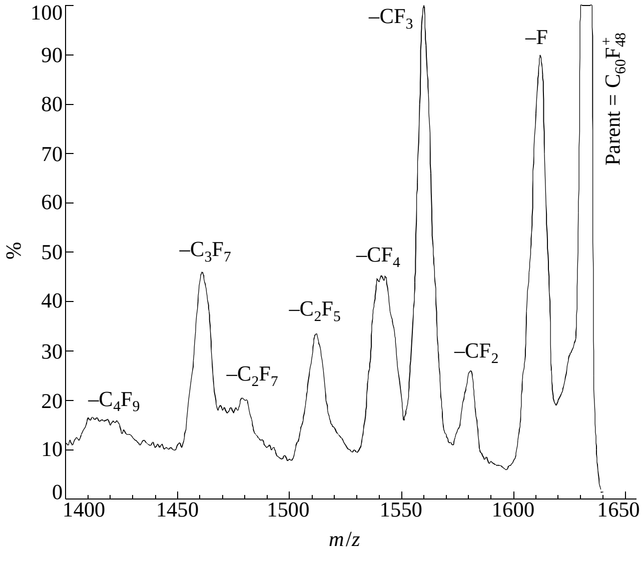

Figure 3 CID MIKE spectrum of parent ion $C_{60}F_{48}^+$.

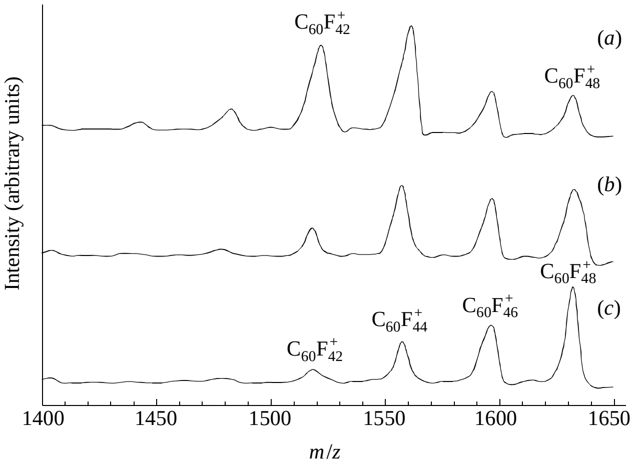

Figure 4 EI mass spectra of sample 1 at 433 K as a function of time, (*a*) initial spectrum; (*b*) after 1.5 h; (*c*) after 3 h.

It is reasonable to assume that formation of $C_{60}F_{2n<48}$ could occur during mass spectrometry analysis due to passivation of the surface of the nickel effusion chamber (according to our observations, fluorofullerenes behave similarly in the platinum effusion cell). Similar processes involving the evaporation of some inorganic fluorides are well known to be accompanied by interaction with the sample holder and formation of fluorides in a lower oxidation state.[7]

Another possibility involves reaction of $C_{60}F_{48}$ with traces of water absorbed on the surface of the sample. A nucleophilic substitution reaction was found to result in the formation of both oxyfluorides and fluorides with lower fluorine content.[8]

Thus, we assume that the effect of the initial drastic change in the mass spectrum of $C_{60}F_{48}$ at constant temperature could be caused by: evaporation of minor impurities of underfluorinated species, a passivation process, or reaction of $C_{60}F_{48}$ with traces of adsorbed water.

In conclusion, the first observation of the mass spectrum of $C_{60}F_{48}$ molecule under KCMS conditions reported, and the KCMS technique is shown to be well suited for quantitative analysis of fluorofullerenes.

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