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Strong fragmentation processes driven by low energy electron attachment to various small perfluoroether molecules

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ABSTRACT

Negative ion formation in the three perfluoroethers (PFEs) diglyme ($C_6F_{14}O_3$), triglyme ($C_8F_{18}O_4$) and crownether ($C_{10}F_{20}O_5$) is studied following electron attachment in the range from ~0 to 15 eV. All three compounds show intense low energy resonances at subexcitation energies (<3 eV) decomposing into a variety of negatively charged fragments. These fragment ions are generated via dissociative electron attachment (DEA), partly originating from sequential decompositions on the metastable (μs) time scale as observed from the MIKE (metastable induced kinetic energy) scans. Only in perfluorocrownether a signal due to the non-decomposed parent anion is observed. Additional and comparatively weaker resonances are located in the energy range between ~10 and 17 eV which preferentially decompose into lighter ions. It is suggested that specific features of perfluoropolyethers (PFPEs) relevant in applications, *e.g.*, the strong bonding to surfaces induced by UV radiation of the substrate or degradation of PFPE films in computer hard disc drives can be explained by their pronounced sensitivity towards low energy electrons.

1. Introduction

Reactions in the three compounds perfluorodiglyme (PD, diethylene glycol dimethyl ether, $C_6F_{14}O_3$), perfluorotriglyme (PT, triethylene glycol dimethyl ether, $C_8F_{18}O_4$), and perfluorocrownether (PC, eicosafluoro-15-crown-5 ether) triggered by resonant attachment of low energy electrons (0–15 eV) are studied in a crossed electron-molecular beam experiment. The molecular structure of the three perfluorocompounds is depicted in Fig. 1. We find that all three molecules exhibit intense resonances at low energies (<3 eV) which decompose into a variety of negatively charged fragments (and their complementary neutral counterparts). Among the three perfluoroethers (PFEs) only crownether shows an ion signal due to a long-lived, non-fragmented parent ion.

Larger oligomeric perfluoropolyethers (PFPEs) like Krytox, Demnum, and Fomblin are well known for many hi-tech applications particularly as excellent lubricants [1]. Due to their high thermal resistance and chemical inertness they are also used as dielectric fluids and as working medium in mechanical pumps and diffusion pumps [2]. PFPEs do not decompose under UV radiation [3] while under electron bombardment positive ions can be observed above an energy threshold of 14 eV [4]. The mechanisms for radiolysis of PFPEs by high energy ionizing radiation were reviewed previously [5]. Secondary ion mass spectrometry with atomic ions and electrons as projectiles with energies in the keV range showed the production of a variety of fragment cations formed by ionization and fragment anions formed by capture of secondary electrons [6–8]. Previously also a MALDI study was carried out with PFPEs in spite of the experimental difficulty that commonly used matrices do not efficiently desorb/ionize fluorinated polymers [9].

PFPE films usually show small adhesion to most surfaces, they can, however, strongly be fixed to a variety of substrates such as carbon, silica and gold under irradiation of the substrate with ionizing radiation [10] and moreover, 172 nm and 185 nm UV light [11,12]. The attached PFPE films do not even rinse off the substrate by fluorinated solvents. Since UV light at 254 nm, where the photon energy was below the work function of the used substrate, did not lead to such an effect, it was suggested [3] that low energy electrons formed by photoemission from the substrate are responsible for the chemical change. This suggestion was in fact supported by further experiments in which the PFPE films were directly exposed to low energy electrons in the range of 2–18 eV, which also resulted in a strong bonding to the surface [3]. It was proposed that low energy electrons generate F^- plus the corresponding radical via DEA as the dominant pathway. Radical propagation and termination then cross-link the polymer resulting in a strong bonding to the surface.

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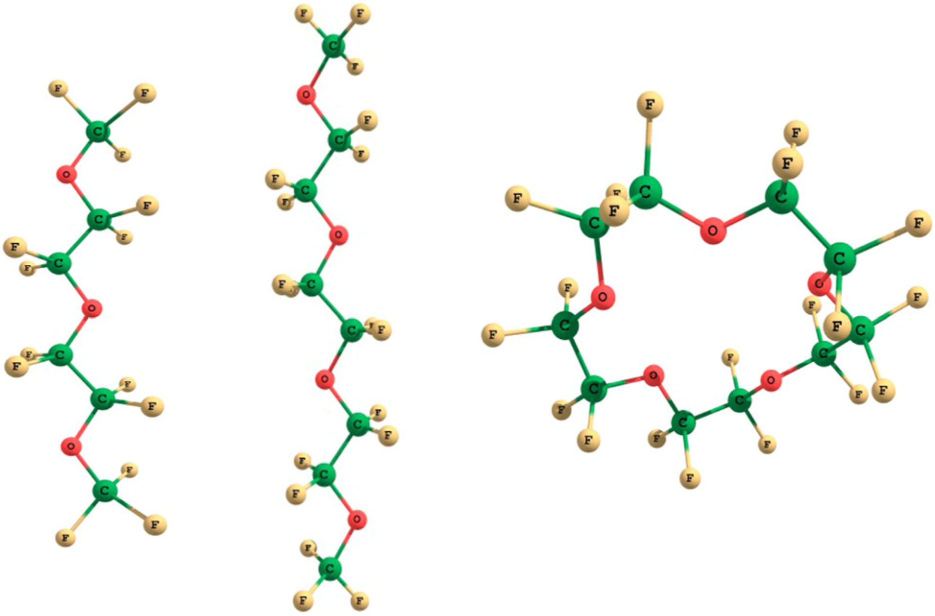

Fig. 1. Molecular structures of perfluorodiglyme (PD), left, perfluorotriglyme (PT), middle, and perfluorocrownether (PC) right, respectively.

However, this proposed mechanism was questioned in [13], where UV induced photodissociation processes were favoured for example due to the observation of bonding even for 254 nm UV light in contrast to previous studies (see detailed discussion in [14]). Moreover, it should be noted that chemical bonding was also observed by irradiation even with visible laser light at 532 nm [15], i.e., using the same argumentation like for the 254 nm UV experiments, another mechanisms other than DEA are also operative to induce chemical bonding.

As will be shown here, the PFPEs are in fact strong electron scavengers. Among the many DEA reactions leading to a variety of negatively charged fragments, the formation F^-, however, is very weak.

Another interesting question in relation to PFPE films concerns tribo-physicochemical phenomena at the oil-lubricated sliding contacts. In that context the degradation of PFPE lubrication on computer hard disc drives was accounted to a microplasma which is generated in the gap of the sliding contact [16]. In computer hard disc drives, the disc surface is coated with a PFPE film and the distance between disc and head is in the order of some tens of nanometres which results in frequent contact between head and disc. It was suggested that a microplasma is generated by the intense electric field caused by tribocharging and it is believed that this microplasma is responsible for the degradation of the PFPE lubricant. In the meantime, much work has been devoted to explore the properties of such tribo-microplasmas generated in oil-lubricated sliding contacts. It has been found, *e.g.*, that PFPE lubricated sliding contacts emit positive ions and electrons but also photons at wavelengths ranging from the UV to the IR [17]. Among these plasma components, the electrons might be responsible for the degradation of the PFPE films thereby reducing the lifetime of hard disc drives. Another study suggested that low energy electrons are produced at the tribological interface and subsequently cause decomposition of PFPEs [18].

Here we explicitly study the reactions of three PFEs with lower molecular weight, induced by low energy electrons. The presently studied molecules can be considered as model systems for oligomeric PFPEs with larger molecular weight. It is shown that all three compounds undergo surprisingly rich fragmentation reactions generating a variety of negatively charged fragment ions (plus the neutral counterparts) within resonances at subexcitation energies (<3 eV) and also within a comparatively weaker resonance in the energy range between about 11 and 17 eV.

2. Experimental

The experiments were performed on a double focusing two sector field mass spectrometer (VG-ZAB2-SEQ) of reversed Nier–Johnson type BE geometry as described previously [19]. The liquid samples possess sufficient vapour pressure so that they were introduced directly into the collision chamber of a Nier-type ion source where the interaction of the neutral effusive molecular beam and the low energy electrons took place. The entire ion source was heated to about 180 °C to avoid contamination of the surfaces. The electron current used was about 10 μA at an electron energy resolution (FWHM) of about 1 eV. The anions formed in the ion source were extracted by a weak electric field and then accelerated to 7 keV into the mass spectrometer. After passing the first field free region, the ions were analysed according to mass (m/e) and momentum by a magnetic sector field B, then pass a second field-free region, until they were finally transmitted through an 81° electric sector field to the channeltron-type detector operated in the single pulse counting regime. The nominal maximal mass resolution of the mass spectrometer is 125,000 (10% valley definition). However, to achieve a better sensitivity, the entrance slit and exit slit of the mass spectrometer were opened which lowered the resolution to about 1000.

The present study was carried out applying two different measurement techniques, (i) negative ion mass spectra were recorded at fixed electron energies and (ii) the mass spectrometer was set to a certain mass and the corresponding ion yield was recorded as a function of the electron energy in the range from about 0 eV up to about 20 eV. In addition, information on metastable decays of ions was obtained, i.e., ions decomposing in the zone between the magnetic and electrostatic analyser thus having a lifetime in the metastable (microsecond) time range. If a selected ion decays into a daughter ion, this daughter ion has the same velocity, but a different kinetic energy. By scanning the voltage of the electrostatic energy analyser, one obtains information on the decomposition of a selected ion. From the shape of these peaks additional informa-

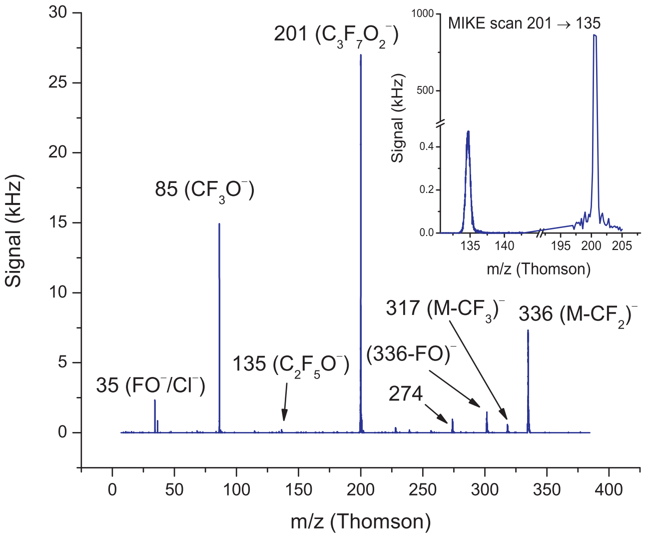

Fig. 2. Negative ion mass spectrum of perfluorodiglyme (PD, $M = 386$ amu) recorded at an electron energy close to zero eV. The inset shows the MIKE scan for the metastable decay of $C_3F_7O_2^-$ (201 amu) into $C_2F_5O^-$ (135 amu) recorded at the electron energy of 1 eV.

tion can be extracted on the kinetic energy release of the daughter ions due to the metastable decomposition and hence this technique is assigned as metastable induced kinetic energy (MIKE) spectroscopy.

The energy scale was calibrated with the peak position of SF_6^- which is formed within a narrow resonance at an energy close to zero eV. The PFEs were purchased from Exfluor Research Corporation (USA) at stated purities of 98% for PD and PT and 99% for PC and used as delivered.

3. Results and discussion

In Figs. 2–4 we present the negative ion mass spectra recorded at low electron energy illustrating the rich fragmentation pattern in each of the three compounds. Only crownether shows an additional, but comparatively weak signal due to the formation of the long lived non-fragmented parent anion (Fig. 4). The mass spectra exhibit some periodicity due to the loss of particular neutral units from the respective transient anion, which will be discussed in some more detail below.

Fig. 5 shows the total ion yield as a function of the electron energy for the three compounds and in Figs. 6–8 the ion yields of a series of selected anionic products are plotted. All yields exhibit pronounced resonance profiles at low energy, in some fragment yield curves an additional feature appears in the energy range between 11 and 17 eV. One can hence assume that the corresponding reactions are triggered by resonant electron attachment, *viz.*,

$$e^- + M \rightarrow M^{-\#} \quad (1a)$$

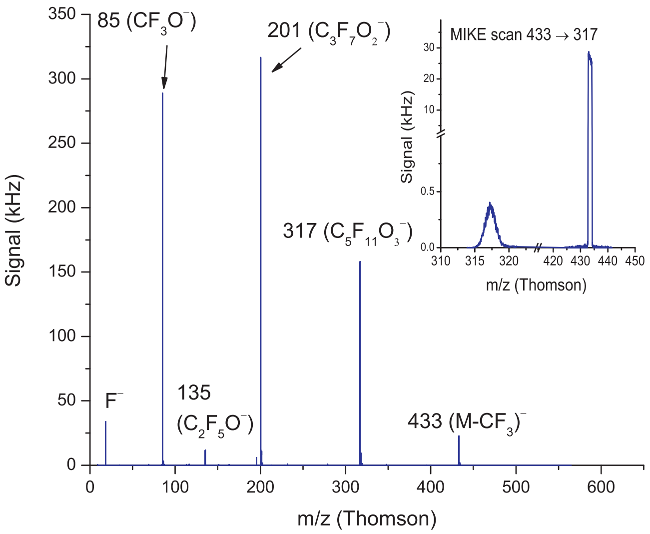

Fig. 3. Negative ion mass spectrum of perfluorotriglyme (PT, $M = 502$ amu) recorded at an electron energy of 4 eV. The inset shows the MIKE scan for the metastable decay of $(M\text{-}CF_3)^-$ (433 amu) into $C_5F_{11}O_3^-$ (317 amu) recorded at the electron energy of 3 eV.

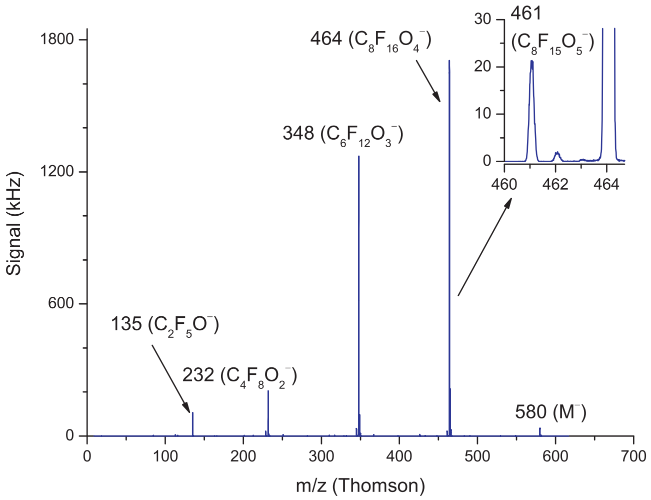

Fig. 4. Negative ion mass spectrum of perfluorocrownether (PC, $M = 580$ amu) recorded at an electron energy of 3.7 eV.

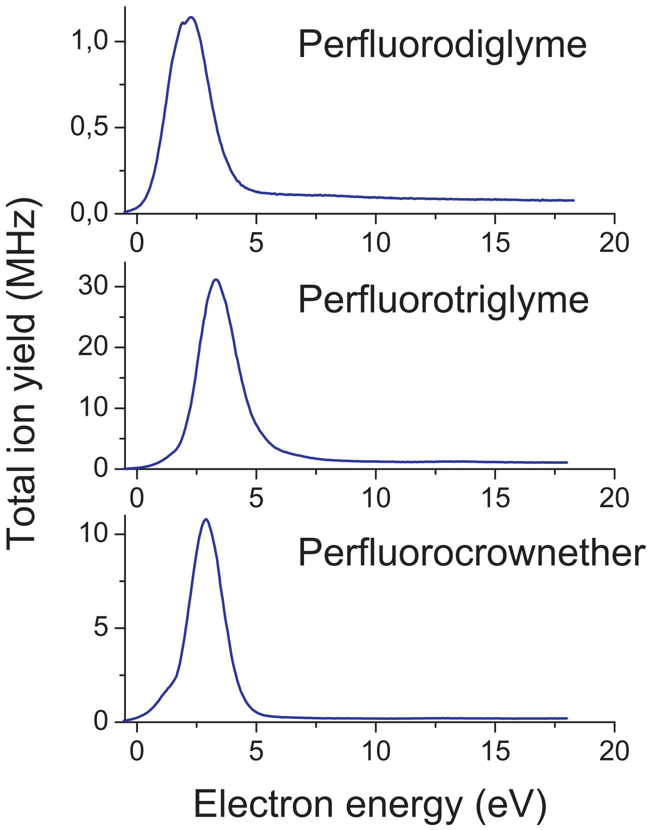

Fig. 5. Total ion yield for the three compounds as a function of the electron energy.

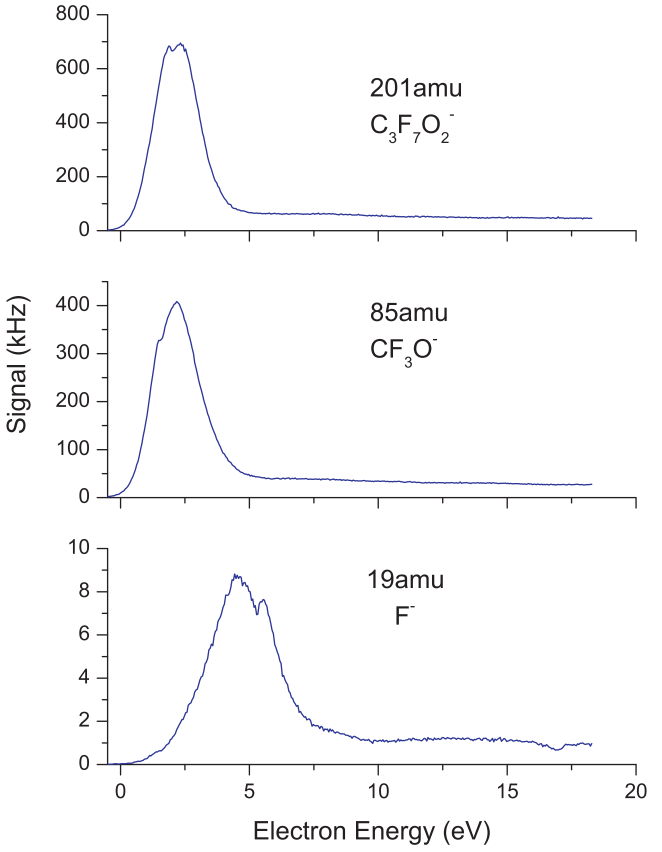

Fig. 6. Ion yield curves for 3 selected fragment ions from perfluorodiglyme (see the text).

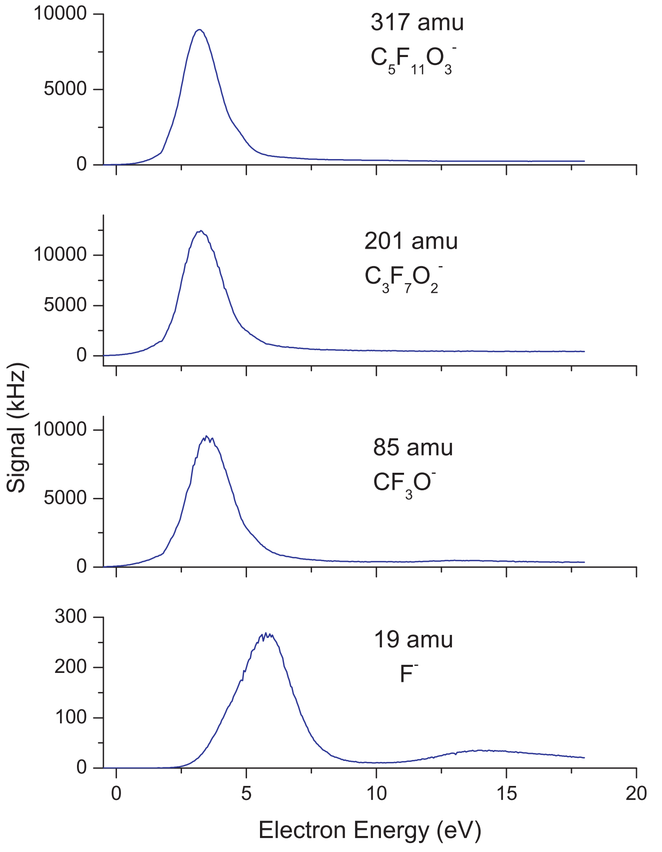

Fig. 7. Ion yield curves for 4 selected fragment ions from perfluorotriglyme (see the text).

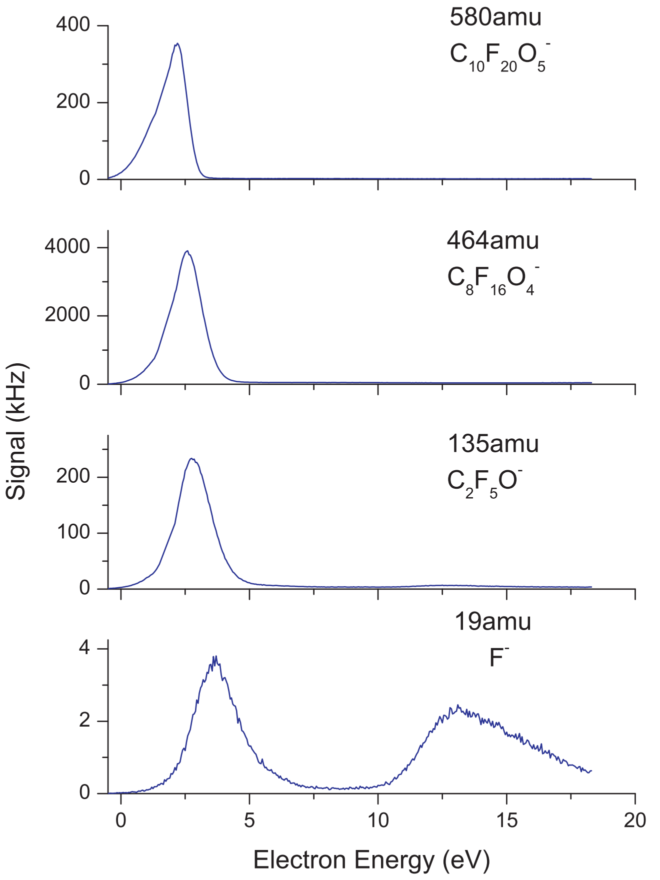

Fig. 8. Ion yield curves for 4 selected fragment ions from perfluorocrownether (see the text).

where M represents the neutral molecule and $M^{-\#}$ the transient negative ion (TNI) formed by electron capture. Such a transient ion state can be considered as a quantum state (or scattering state) embedded in the continuum represented by the target molecule and the extra electron at rest at infinity. While the electron is temporarily bound by short range forces, the *total* energy of the TNI is *above* that of the neutral molecule and hence it is principally unstable towards the loss of the extra electron (autodetachment) thereby recovering the neutral molecule. In the case when decomposition products are energetically accessible within the energy of the TNI, it may decompose into a negatively charged and one or more neutral fragments according to

$$M^{-\#} \rightarrow R + X^- \tag{1b}$$

The entire two step process (1a) and (1b) is known as resonant dissociative electron attachment (DEA) [20,21]. For the present compounds a variety of such DEA reactions are apparently accessible at very low energies. Perfluorocompounds are particularly interesting as they often form long-lived anions by capture of *free* electrons at very low energy under single collision conditions. Representative members are C_6F_6 and SF_6 which both very effectively capture electrons at energies close to zero to form a long lived parent anions which can be observed by mass spectrometry [22,23]. Their long lifetime is a result of effective transfer of electronic energy into vibrational energy thereby delaying autodetachment [20–23]. In these two compounds, on the other hand, low energy DEA channels are not accessible so that autodetachment is the only decay mechanism. In contrast to that in the present PFE molecules, various low energy DEA channels are accessible and only in crownether we observe a non-fragmented parent anion which may be the consequence of a delicate balance between autodetachment and unimolecular decomposition. In that respect, the PFEs behave similar to explosives like TNT (trinitrotoluol) [24]. From the MIKE scans it also follows, that sequential unimolecular decompositions on the metastable time scale (μs) contribute to the negative ion mass spectra in addition to the prompt dissociation occurring in the ion source (see below).

3.1. Negative ion mass spectra

3.1.1. Perfluorodiglyme ($C_6F_{14}O_3$, 386 amu)

Fig. 2 presents the negative ion mass spectrum recorded at an electron energy close to zero energy. The strong signal at 336 amu corresponds to an ion with the stoichiometric composition $C_5F_{12}O_3^-$ which arises from the loss of a neutral CF_2 unit from the parent anion yielding $(M\text{-}CF_2)^-$. The signal at 301 amu can be assigned to an additional loss of an FO unit yielding $(M\text{-}CF_3O)^-$ or $C_5F_{11}O_2^-$.

From the mass spectrum it is not directly obvious to which degree these reactions are direct (prompt) or sequential, i.e., first loss of CF_2 and subsequent loss of FO (from $(M\text{-}CF_2)^-$) or direct loss of a terminal CF_3O unit from the TNI. The peak at 274 amu remains unassigned since no stoichiometric composition of a fragment anion of perfluorodiglyme coincides with this mass and therefore we ascribe the yield to an impurity. The strong signal at 201 amu can be assigned to an ion of the stoichiometric composition $C_3F_7O_2^-$ which corresponds to the loss of one terminal CF_3O unit and two CF_2 units, or equivalently, the loss of a terminal CF_3 group and the loss of a CF_2–CF_2–O unit with the remaining ion being CF_3–O–CF_2–CF_2–O^-. The peak at 85 amu is identified as CF_3O^-, representing the terminal unit of linear chain. This anion possesses a remarkably strong binding energy for the excess electron (electron affinity of the corresponding radical) of 4.4 eV [25]. A further signal is observed at 35 amu which can be assigned to either Cl^- (arising from DEA to some spurious background of Cl containing 1,3-dichloroacetone measured previously) or the diatomic anion FO^-. From the isotope ratio $^{35}Cl/^{37}Cl$ it can be concluded that the signal at 35 amu contains 60% $^{35}Cl^-$ and 40% FO^-. The latter ion is known as a stable diatomic species having a binding energy of 2.27 eV [26] for the excess electron. It must be formed within a rather complex sequence involving the cleavage of two C–O bonds and one C–F bond and formation of FO^- with the excess charge remaining on the final product. The fragment F^- is also formed, but at comparably low intensity and also at higher energies and is hence not visible on the mass spectrum taken close to zero eV.

We have also recorded MIKE scans yielding information on metastable decays of ions which also depends on the primary electron energy defining the excess energy of the TNI. We find that at an electron energy of 6 eV the fragment ion $C_5F_{11}O_3^-$ (317 amu, visible as a small peak in the mass spectrum taken close to zero energy) decomposes by the loss of neutral CF_2–CF_2–O unit (116 amu) into $C_3F_7O_2^-$ (201 amu) and the loss of $C_3F_6O_2$ (182 amu) into $C_2F_5O^-$ and at 1 eV electron energy the ion $C_3F_7O_2^-$ (201 amu) undergoes metastable decomposition by the loss of CF_2O (66 amu) into $C_2F_5O^-$ (135 amu). The MIKE spectrum for the latter decay is shown as inset in Fig. 2. The MIKE scans indicate that $C_2F_5O^-$, which is formed in a sequential decay, has different precursor anions depending on the initial electron energy. The overall abundance of $C_2F_5O^-$ in the mass spectra is however low, i.e. $C_2F_5O^-$ may be an unstable intermediate product in the sequential decay leading to CF_3O^- or FO^-.

The decomposition of PD hence occurs by the loss of various units (directly and/or sequentially) leading to a series of anions while DEA into F^- is a comparably ineffective reaction.

3.1.2. Perfluorotriglyme ($C_8F_{18}O_4$, 502 amu)

This compound is formally formed from perfluorodiglyme by just adding one ether unit (CF_2–O–CF_2) into the chain of the linear molecule. Interestingly, the ion with highest mass number observed in Fig. 3 is 433 amu corresponding to the loss of a neutral CF_3 unit, yielding the ion $(M\text{-}CF_3)^-$ or $C_7F_{15}O_4^-$ while in PD it is the loss of CF_2 and the loss of CF_3 is much weaker. The subsequent mass numbers on the scale downwards are 317, 201, and 85 amu which are in each case formed by the loss of an additional (CF_2–CF_2–O) unit or after molecular rearrangement an additional ether unit (CF_2–O–CF_2) arriving at 85 amu which is assigned as CF_3O^- representing the terminal unit of the linear chain as above. The comparably smaller peak at 135 amu is identified as the anion of perfluorodimethylether CF_3–O–CF_2^-. The lowest mass peak is found at 19 amu and is ascribed to F^-.

From the MIKE scans we find metastable decompositions of the ion at 433 amu $(M\text{-}CF_3)^-$ to the ion at 317 amu (shown in the inset in Fig. 3; loss of CF_2–CF_2–O and operative in an electron energy range between 3 and 10 eV), a metastable decomposition of $C_3F_7O_2^-$ (201 amu) into CF_3O^- (85 amu) (loss of a CF_2–CF_2–O unit observed at 3 eV electron energy) and finally a metastable decomposition of CF_3–O–CF_2^- (135 amu) into CF_3O^- (85 amu) (loss of a CF_2), observed at 3.5 eV electron energy. In contrast, the metastable decay of $C_3F_7O_2^-$ in the case of PD leads exclusively to the formation of $C_2F_5O^-$, which for PT seems not to be a product from $C_3F_7O_2^-$ in a sequential decay.

3.1.3. Perfluorocrownether ($C_{10}F_{20}O_5$, 580 amu)

As can be seen from Fig. 4 the negative ion mass spectrum of PC contains a signal at 580 amu due to the non-fragmented parent anion. We note that by the present experiment we cannot distinguish if the structure of the parent anion is still cyclic or we have the case of a linear distonic anion which underwent one bond cleavage. On the mass scale downwards, the subsequent strong peaks at 464, 348 and 232 amu can be assigned to ions formed by the loss of one, two, and three neutral CF_2–O–CF_2 (or CF_2–CF_2–O) units (116 amu), respectively, finally arriving at 232 amu which is identified as $C_4F_8O_2^-$ with the possible structure CF_2–O–CF_2–CF_2–O–CF_2 (or CF_2–CF_2–O–CF_2–CF_2–O). The further strong peak at 135 amu is, as above, identified as the anion of perfluorodimethylether CF_3–O–CF_2^-. This anion may be formed via a rather complex reaction sequence involving multiple bond cleavages, transfer of an F atom and formation of a C–F bond.

In the mass spectrum (Fig. 4) one can identify small but distinct satellite peaks below the dominant mass peaks at 464, 348, and 232 amu, see inset in Fig. 4. These satellite peaks are located three mass units below the corresponding strong peaks, the latter corresponding to the subsequent loss of CF_2–CF_2–O units starting at parent anion (580 amu). The satellite peaks then correspond to the fragmentation channel with initial loss of C_2F_4 + F or C_2F_5, i.e., the pentafluoro ethyl radical formed upon rearrangement, from the parent anion.

From the MIKE scans we identify a metastable decomposition from the parent anion (580 amu) to the ion at 464 amu (loss of C_2F_4O), and the ion at 348 amu (loss of two C_2F_4O units), both metastable decompositions are operative at electron energies below about 4 eV. Further metastable decompositions are identified from the ion at 464 amu ($C_8F_{16}O_4^-$ or $(M\text{-}(C_2F_4O))^-$) into the ion at 348 amu (loss of C_2F_4O), and for the ion at 348 amu ($C_6F_{12}O_3^-$) to the ion at 232 amu (again loss of C_2F_4O). Both metastable decompositions are operative at electron energies below about 4 eV. Thus $C_6F_{12}O_3^-$ is formed in a direct decay from the parent anion as well in a sequential decay via $C_8F_{16}O_4^-$.

3.2. Ion yields

Fig. 5 presents the total anion yield for the three perfluorocompounds. Figs. 6–8 show the yields of some individual ions indicating that ions are predominantly formed in the energy range below

5 eV. The individual ion yields, however, indicate an additional resonance feature in the range 11–17 eV which is particularly visible on the F^- yield. From the mass spectra it is obvious that in the three perfluoro-compounds most of the ion intensity following electron capture is channelled into fragment ions generated by the loss of larger units like CF_2–CF_2–O etc.

Owing to the poor electron energy resolution it is not clear whether the low energy features in the three molecules are composed of different resonances. In any case, at energies below about 4 eV, transient anions can be characterised as shape resonances, formed by accommodation of the extra electron in one of the empty molecular orbitals (MOs). In the present compounds the involved MOs would be composed of antibonding σ^*(C–O) or σ^*(C–F) components. Calculated MO energies of the studied compounds are not available and can be found in literature only for related PFEs [27] (basing on semi-empirical models). At very low energy and in particular in larger molecules, electrons can also be bound by weak polarisation forces, accompanied by effective transfer of electronic into vibrational energy (vibrational Feshbach resonances [28]). In the energy range around 11–17 eV it is likely that core excited resonances dominate with possible contributions of higher lying σ^* resonances. In core excited resonances the energetic electron triggers an electronic excitation and is concomitantly trapped in the field of the excited species.

3.2.1. Perfluorodiglyme ($C_6F_{14}O_3$, 386 amu)

Fig. 6 shows the ion yields of the intense fragment ions $C_3F_7O_2^-$ (201 amu) and CF_3O^- (85 amu) and for comparison the yield of the comparatively much weaker F^- ion. The ion CF_3O^- is most likely due to a simple C–O bond cleavage yielding the neutral complement $C_5F_{11}O_2$.

We shall not discuss the energetic situation in any great detail due to the poor energy resolution. In addition, for most of the fragments involved, there are no thermodynamic data available in the literature. We shall instead illustrate the energetic situation on behalf of two prototype reactions, namely formation of CF_3O^- and formation of F^- (from PD and PT).

The thermodynamic threshold (ΔH_0) of a dissociative electron attachment reaction leading to an anion (X^-) and a neutral fragment (R) can be expressed as

$$\Delta H_0 = D(\mathrm{R}-\mathrm{X}) - \mathrm{EA}(\mathrm{X}) \qquad (2)$$

with D the bond dissociation enthalpy between R and X and EA(X) the electron affinity of fragment X. The C–O binding enthalpy is not explicitly known for the present molecules, but one can estimate from available thermodynamical data [29–31] the C–O bond dissociation enthalpy in dimethylether as 3.8 eV and use this value as a rough estimate for the C–O bond dissociation enthalpy in PD or PT. The electron affinity for CF_3O is 4.4 eV [25], it hence more than counterbalances the C–O bond dissociation enthalpy and we arrive at an exothermicity of $\Delta H_0 = -0.6$ eV for the reaction generating CF_3O^- and the corresponding neutral radical. The formation of the abundant ion at 201 amu ($C_3F_7O_2^-$) may imply similar energetics but for this compound no information on the electron affinity is available.

F^- is formed at significantly higher energies which mirrors the different energetic situation: Typical C–F binding energies are in the range 4.5–5.5 eV [29–31] which is larger than the electron affinity of F (3.40 eV) and hence the formation of F^- is endothermic by 1–2 eV.

3.2.2. Perfluorotriglyme ($C_8F_{18}O_4$, 502 amu)

Most of the ion yields generated from this compound show resonance profiles peaking near 3 eV like that of the ion at 317 amu ($C_5F_{11}O_3^-$), the dominant anion at 201 amu ($C_3F_7O_2^-$) and at 85 amu (CF_3O^-) (see Fig. 7). The F^- yield (Fig. 7 bottom) is located near 6 eV. In terms of molecular orbitals (MOs) this may be interpreted by localized σ^*(C–F) MOs near 6 eV and more delocalised MOs located near 3 eV generating the various other fragments. In both the CF_3O^- and F^- ion yields resonant contributions in the energy range between 11 and 17 eV are visible. It is likely that these core excited resonances decompose into more than two fragments. It should also be noted that these negative ion states are partly located in the ionisation continuum of the molecule and hence represent so called super excited states.

3.2.3. Perfluorocrownether ($C_{10}F_{20}O_5$, 580 amu)

In contrast to PD and PT, perfluorocrownether (PC) exhibits a significant signal due to the non-fragmented parent anion which is formed within a resonant feature peaking near 2 eV (see Fig. 8). If parent anions are observed at all by free electron attachment, they are often formed at very low energies (close to zero eV) like the prototype molecules SF_6 and C_6F_6 and other perfluorinated compounds [20–23,31]. A few reports also exist on molecules, which do form long lived parent anions off zero energy like in p-benzoquinone at 1.4 eV [32–35], azobenzene at 0.9 and 1.2 eV [36] and pyromellitic acide amide at 1.65 eV [37]. Electron attachment to C_{60} is a particular case generating C_{60}^- over a wide and structured feature from threshold (0 eV) to about 12 eV [38–41]. C_{60} is a highly symmetric compound with equal binding energies for each C atom thereby providing ideal conditions for a delayed autodetachment resulting in a situation that C_{60}^- can be observed on the mass spectrometric time scale at attachment energies up to 12 eV.

In the present case we have a situation that fragment ions and the parent ion are observed within the same electron energy range. It is hence a delicate balance between the lifetime of the parent anion (with respect to autodetachment) and the time it takes to fragment into the various DEA channels which controls the visibility of the parent ion on the mass spectrometric time scale. Fig. 8 also shows the ion yield for the fragment ion due to the loss of one C_2F_4O unit at 464 amu which is representative for all the other intense fragments.

From Figs. 6–8 it can be seen that the lighter ions F^-, CF_3O^- from PT or $C_2F_5O^-$ from PC also arise from the resonance feature at higher energy which is particularly pronounced in the F^- yield from perfluorocrownether (Fig. 8).

Such behaviour can be explained by the probability of distributing the excess energy among the fragments. In recording the heavy ion like that at 464 amu arising from PC, most of the available excess energy (essentially the electron energy) will be distributed to this heavy ion which above some threshold will become thermodynamically unstable (with respect to dissociation *and* loss of the excess charge). This makes it unlikely that the large ion is observed in the energy range between 11 and 17 eV. In contrast, in recording the light fragment ion F^-, most of the excess energy will be carried by the large neutral complement, which may undergo further decomposition reactions and there are hence no restrictions for the observation of F^-.

4. Conclusion

All three perfluoroethers are sensitive towards subexcitation electrons thereby decomposing by the loss of neutral CF_2, CF_3 and CF_2–O–CF_2 or CF_2–CF_2–O units into a variety of negatively charged ions and their neutral counterparts. We also identified a series of metastable decays indicating that prompt (direct) but also sequential decompositions in the metastable (μs) time scale contribute to the observed negative ion mass spectra. Only perfluorocrownether shows a signal due to the non-fragmented parent anion. Dissociative electron attachment into F^- is comparatively weak. The present results support the picture that low energy electrons generated in tribo-micro-plasmas are responsible for the degradation of PFPE films on computer hard disc drives and that low energy electrons can contribute to the bonding of PFPE films under UV irradiation of the substrate.

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References

[1] J. Scheirs, Perfluoropolyethers (synthesis, characterization and applications) , in: J. Scheirs (Ed.), Modern Fluoropolymers, John Wiley & Sons, Ltd, 1997.
[2] L. Holland, L. Laurenson, R.E. Hurley, K. Williams, Nucl. Instrum. Methods 111 (1973) 555.
[3] G.H. Vurens, C.S. Gudeman, L.J. Lin, J.S. Foster, Langmuir 8 (1992) 1165.
[4] E. D'Anna, G. Leggieri, A. Luches, A. Perrone, J. Vac. Sci. Technol. A 5 (1987) 3436.
[5] A. Faucitano, A. Buttafava, S. Karolczak, P.A. Guarda, G. Marchionni, J. Fluorine Chem. 125 (2004) 221, and references mentioned therein.
[6] A.M. Spool, P.H. Kasai, Macromolecules 29 (1996) 1691.
[7] P.H. Kasai, A.M. Spool, J. Phys. Chem. B 102 (1998) 7331.
[8] J.M.C. Lourenco, R.T. Carrapa, O.M.N. Teodoro, A.M.C. Moutinho, M.A. Gleeson, J. Los, A.W. Kleyn, Chem. Phys. Lett. 336 (2001) 431.
[9] A. Marie, S. Alves, F. Fournier, J.C. Tabet, Anal. Chem. 75 (2003) 1294.
[10] T.H.D. Lee, J. Vac. Sci. Technol. A 9 (1991) 1287.
[11] H. Chiba, N. Nakamura, M. Takeda, K. Watanabe, IEEE Trans. Magn. 38 (2002) 2108.
[12] D. Saperstein, L.J. Lin, Langmuir 6 (1990) 1522.
[13] R.J. Waltman, X.-C. Guo, Tribol. Lett. 27 (2007) 227.
[14] X.-C. Guo, R.J. Waltman, Langmuir 23 (2007) 4293.
[15] L. Zhu, J. Zhang, T. Liew, K.D. Ye, J. Vac. Sci Technol. A 21 (2003) 1087.
[16] K. Nakayama, S.M.D. Mirza, Tribol. Trans. 49 (2006) 17.
[17] K. Nakayama, J. Phys. D: Appl. Phys. 40 (2007) 1103.
[18] Z. Zhao, B. Bhushan, C. Kajdas, Tribol. Lett. 6 (1999) 141.
[19] D. Huber, M. Beikircher, S. Denifl, F. Zappa, S. Matejcik, A. Bacher, V. Grill, T.D. Märk, P. Scheier, J. Chem. Phys. 125 (2006) 084304.
[20] E. Illenberger, J. Momigny, Gaseous Molecular Ions. An Introduction to Elementary Processes Induced by Ionization, Steinkopff, Darmstadt , Springer, New York, 1992.
[21] L.G. Christophorou, Electron-Molecule Interactions and Their Applications, vol. I, Academic Press, Orlando, 1984.
[22] R. Balog, J. Langer, S. Gohlke, M. Stano, H. Abdoul-Carime, E. Illenberger, Int. J. Mass Spectrom. 233 (2004) 267.
[23] M. Fenzlaff, E. Illenberger, Chem. Phys. 136 (1989) 443.
[24] P. Sulzer, F. Rondino, S. Ptasinska, E. Illenberger, T.D. Märk, P. Scheier, Int. J. Mass Spectrom. 272 (2008) 149.
[25] L.G. Huey, E.J. Dunlea, C.J. Howard, J. Phys. Chem. 100 (1996) 6504.
[26] M.K. Gilles, M.L. Polak, W.C. Lineberger, J. Chem. Phys. 96 (1992) 8012.
[27] S. Matsunuma, Y. Hose, Tribol. Int. 30 (1997) 121.
[28] H. Hotop, M.-W. Ruf, M. Allan, I.I. Fabrikant, Adv. At. Mol. Opt. Phys. 49 (2003) 85.
[29] The NIST Chemistry WebbBook: http://webbook.nist.gov/.
[30] D.R. Lide (Ed.), Handbook of Chemistry and Physics, 78th ed., CRC Press, Boca Raton, 1997.
[31] S. Feil, T.D. Märk, A. Mauracher, P. Scheier, C.A. Mayhew, Int. J. Mass Spectrom. 277 (2008) 41.
[32] D.F. McMillen, D.M. Golden, Ann. Rev. Phys. Chem. 33 (1982) 493.
[33] L.G. Christophorou, J.G. Carter, A.A. Christodoulides, Chem. Phys. Lett. 3 (1969) 237.
[34] C.D. Cooper, W.T. Naff, R.N. Compton, J. Chem. Phys. 63 (1975) 2752.
[35] M. Allan, Chem. Phys. 81 (1983) 235.
[36] Y.V. Vasil'ev, V.A. Mazunov, E.R. Nazirov, Org. Mass Spectrom. 26 (1991) 739.
[37] O.G. Khvostenko, G.M. Tuimedov, Rapid Comm. Mass Spectrom. 20 (2006) 3699.
[38] T. Jaffke, E. Illenberger, M. Lezius, St. Matejcik, D. Smith, T.D. Märk, Chem. Phys. Lett. 226 (1994) 213.
[39] S. Matejcik, T.D. Märk, P. Spanel, D. Smith, T. Jaffke, E. Illenberger, J. Chem. Phys. 102 (1995) 2516.
[40] V.S. Prabhudesai, D. Nandi, E. Krishnakumar, Eur. Phys. J. D 35 (2005) 261.
[41] O. Elhamidi, J. Pommier, R. Abouaf, J. Phys. B: At. Mol. Opt. Phys. 30 (1997) 4633.