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Investigations of electron attachment to the perfluorocarbon molecules c-C_4F_8, 2-C_4F_8, 1,3 C_4F_6, and c-C_5F_8

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It is with great respect and considerable gratitude that we dedicate this paper to our colleague and friend Professor Eugen Illenberger on his 65th birthday.

Keywords:
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ABSTRACT

Non-dissociative and dissociative electron attachment to a series of gas-phase perfluorocarbons (PFCs), namely octafluorocyclobutane, c-C_4F_8, octafluorobut-2-ene (perfluoro-2-butene), 2-C_4F_8, hexafluorobuta-1,3-diene (1,3 perfluorobutadiene), 1,3 C_4F_6, and octafluorocyclopentene (perfluorocyclopentene), c-C_5F_8, of importance to technological plasmas, have been investigated using two different, but complimentary, instruments available in Innsbruck over the electron energy range 0–20 eV. Anion yields as a function of electron energy have been recorded, with the positions and intensities of the electron attachment resonances being determined. One of these instruments is a double focusing sector field mass spectrometer (VG-ZAB-2SEQ), which has been used for measurements requiring high sensitivity and for obtaining accurate relative anion yields. It has also been used to determine the electron detachment lifetimes of the parent anions under various accelerating voltages, and these results are also presented. The second instrument (CELIA) is a trochoidal electron monochromator coupled to a quadrupole mass filter with a pulse counting system for detecting product anionic species. This provides a much higher energy resolution than the VG-ZAB, which makes it a better instrument to investigate narrow energy resonances close to 0 eV. The results of anion yields, peak positions and the relative intensities presented in this paper are compared with previous data of electron attachment to the above PFCs, including investigations by Professor Eugen Illenberger.

1. Introduction

1.1. Background

Attachment of low energy (0–20 eV) electrons to molecules (ABC) involves formation of a transient negative ion $(ABC)^{-*}$ which usually dissociates rapidly to lead to the formation of a stable daughter anion and at least one neutral radical:

$$e^- + ABC \rightarrow (ABC)^{-*} \rightarrow A^- + BC \tag{1}$$

This process is known as dissociative electron attachment (DEA) [1]. The parent anion may be observed if the autodetachment lifetime (which depends on molecular size, structure and internal energy) is longer than its transmission time to the detector of the instrument, or if collisional or radiative stabilisation occurs before dissociation occurs. DEA is an important chemical reaction occurring in many diverse physical and chemical environments, ranging from plasma etching through to damage in biological systems.

The objectives of electron attachment studies include: (i) investigations of the effects of molecular structure on electron attachment processes, (ii) to identify the decay channels, in order to provide a deeper understanding of electron capture to molecules, and (iii) to obtain relative cross-sections as a function of electron energy. Towards these goals here we report a detailed study of electron attachment to four perfluorocarbons (PFCs), all of which are of importance to technological plasma applications, and hence fundamental data on electron interactions are required. There are some inconsistencies in the earlier works associated with some of these molecules, e.g., positions and number of resonances, and we wish to resolve these in this paper.

The PFCs used in this investigation are octafluorocyclobutane, c-C_4F_8, octafluorobut-2-ene (perfluoro-2-butene), 2-C_4F_8, hexafluorobuta-1,3-diene (1,3 perfluorobutadiene), 1,3 C_4F_6, and octafluorocyclopentene (perfluorocyclopentene), c-C_5F_8. These molecules have been suggested as possible replacements of SF_6 and fluorocarbons (e.g., CF_4, C_2F_4, C_2F_6 and CH_3F) used in and emitted during technological plasma treatments, because (and with the exception of c-C_4F_8) they have significantly lower greenhouse warming potentials (GWP) than SF_6. (Even for c-C_4F_8, its GWP is approximately a factor of three less than that of SF_6: GWP c-

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$C_4F_8 = 8700 \times CO_2$, compared to GWP $SF_6 = 24{,}000 \times CO_2$—but this still makes it unsuitable as an environmentally viable etching gas.) The replacement of high GWP gases with lower GWP gases would significantly reduce the environmental impact on the use of technological plasmas used in the material industries. Given the above descriptions, the study of electron attachment properties of these PFCs is thus of practical interest relating to the possible optimisation and control of gaseous plasma discharges containing these molecules.

1.2. *Specific molecular systems studied*

Octafluorocyclobutane, *c*-C_4F_8, is an important industrial gas, especially in plasma processing [2–4]. It is used extensively in dry etching processes due to its high selectivity over other fluorocarbon feed gases [2]. It is an important feedstock for plasma etching of silicon dioxide in semiconductor manufacturing. Furthermore, it is also used for high-voltage insulation, especially in *c*-C_4F_8/SF_6 mixtures. Here, the rapid thermal rate coefficient for non-dissociative electron attachment to *c*-C_4F_8 makes it more suitable than other insulating mixtures [5]. Owing to these physical advantages, there have been many studies on the interaction of electrons with *c*-C_4F_8 [5–10]. Despite these numerous studies, there is a lack of agreement, with a number of discrepancies being apparent between the published results. In 1972 a group from Edinburgh (Harland and Thynne) [6] and another group from Israel (Lifshitz and Grajower) [7] presented the first electron capture data over the electron energy range 0–12 eV. Both groups observed the parent anion (at 0 eV) and dissociative channels for the production of F^-, $CF_3{}^-$, and $C_3F_5{}^-$. However, whilst there is reasonable agreement between the two for these dissociative channels in terms of overall structure of the attachment spectra, there are noticeable and rather significant differences in peak positions. Furthermore, for two dissociative channels, leading to F^- and $C_3F_5{}^-$, an additional resonance peak is observed at low electron energies in the work by Lifshitz and Grajower, which is not observed by Harland and Thynne. In addition to this discrepancy, a number of different dissociative electron attachment channels are reported between the two studies. Whereas Lifshitz and Grajower also reported observing $C_2F_3{}^-$, Harland and Thynne did not observe that channel, but did report observing the dissociative channels $F_2{}^-$ and $CF_2{}^-$. A later study by Sauers et al. [9], using time-of-flight mass spectrometry, confirmed the dominance for the formation of the parent anion at zero electron energy. They also reported the dissociative channels of F^-, $CF_3{}^-$, $C_2F_3{}^-$ and $C_3F_5{}^-$, in agreement with the work of Lifshitz and Grajower, but did not observe the additional peak for the production of F^- and $C_3F_5{}^-$, observed at 1.75 eV by Lifshitz and Grajower. Given these differences in the published data, an aim of this current study is to measure with high resolution and high sensitivity low energy electron capture to *c*-C_4F_8 in order to help resolve the discrepancies appearing in the literature.

Octafluorobut-2-ene (perfluoro-2-butene), 2-C_4F_8, has not been as extensively studied as *c*-C_4F_8. Lifshitz and Grajower used the retarding potential difference method to obtain the ionization efficiency curves over the electron energy range of 0–12 eV [7]. Christodoulides et al. studied electron attachment to this molecule in the electron energy range 0–3 eV using electron swarm techniques [11]. Using a time-of-flight mass spectrometer, Sauers et al. studied resonant non-dissociative and dissociative attachment of electrons in the energy range 0–12 eV [9]. Chutjian and Alajajian investigated electron attachment cross-sections in the electron energy range 0–150 meV, at an energy resolution of 5–8 meV, observing only the parent anion over this energy range [12].

Compared to the saturated PFC *c*-C_4F_8, which has a 100 year GWP of 8700, the GWP for 1,3 C_4F_6 is negligible because of its short atmospheric lifetime (calculated to be 1.9 days) [13] and hence is considerably less detrimental to the atmosphere. Therefore, hexafluorobuta-1,3-diene (1,3 perfluorobutadiene), 1,3 C_4F_6, is also a promising choice to replace the greenhouse gas *c*-C_4F_8 as an etchant feed in plasmas. The work by Nakamura et al. has illustrated that this molecule (and *c*-C_5F_8) has good etch properties, and can indeed be used as a good dry-etch gas (line width as narrow as 90 nm), i.e. it provides high etch rates and good profile control [14]. Despite its potential importance to dry-etching processing (e.g., high selectivity and good etch properties), to our knowledge, there have only been two other previous electron capture studies, one by Sauers et al. [9], and the other by Illenberger an co-workers [15]. There observations showed that there is a striking contrast to the fragmentation patterns as compared to the other PFCs they studied. They discovered that the cross-section for the attachment of 0 eV, leading to the parent anion, is small, and that the cross-section for attachment is dominated by high energy resonances leading to dissociative attachment products.

Octafluorocyclopentene (perfluorocyclopentene), *c*-C_5F_8, is emerging as one of the most promising replacement of conventional plasma processing gases, such as CF_4, C_2F_6, and *c*-C_4F_8. This is because of two main factors. Firstly it has high etching selectivity, and secondly it has a low impact on our environment. *c*-C_5F_8 has a GWP of only 100, which is a result of its relatively short atmospheric lifetime of approximately 1 year, making it one of shortest lifetimes among the various proposed PFC alternatives [16,17]. The electron attaching properties of *c*-C_5F_8, have been less extensively studied than the other PFCs of this investigation. Zollars et al. (1984) report a study of the collisions of Xe(*nf*) with *c*-C_5F_8, with rate coefficients being measured and product anions being identified (predominantly $C_5F_8{}^-$, although a small signal attributed to $F_2{}^-$ was also observed) [18]. Earlier swarm measurements (Christophorou [19] and Pai et al. [20]) had shown that *c*-C_5F_8 attach low energy electrons with a large rate coefficient. Fenzlaff and Illenberger [21] have presented an electron beam study in the energy range 0–20 eV. They showed that the attachment is dominated by the formation of the parent at 0 eV, followed by F^- and $C_5F_7{}^-$ at higher electron energies [21]. Later, using electron attachment mass spectrometry, Imai and Tachibana (1999) also recorded the yields of fragment anions resulting from electron attachment as a function of electron energy [17]. Interestingly, they did not observe any parent anion.

This paper is now organized as follows: in the next section we will briefly describe the two instruments used in this study. In Section 3 the experimental results are reported. These include anion mass spectra and anion yields (Sections 3.1–3.4), which are compared to any other previous investigations, and the first measurements of the parent anions electron detachment lifetimes (Section 3.5). We conclude with a brief summary of the key conclusions in Section 4.

2. Experimental

The electron attachment spectrometer in Innsbruck (CELIA) consists of a molecular beam system, a trochoidal electron monochromator (TEM) and a quadrupole mass filter with a pulse counting system for detecting product ionic species [22]. For the set of experiments presented here the TEM was operated with an energy resolution of about 0.10 eV as a compromise between product ion intensity and incident electron energy resolution. The gas of interest was expanded at a pressure of about 10 mbar through a 20 μm nozzle into the attachment region, and the whole apparatus was kept at a constant temperature before and during the measurements of about 328 K. The electron beam intersected an effusive beam of the neutral molecules at right angles. The product anions

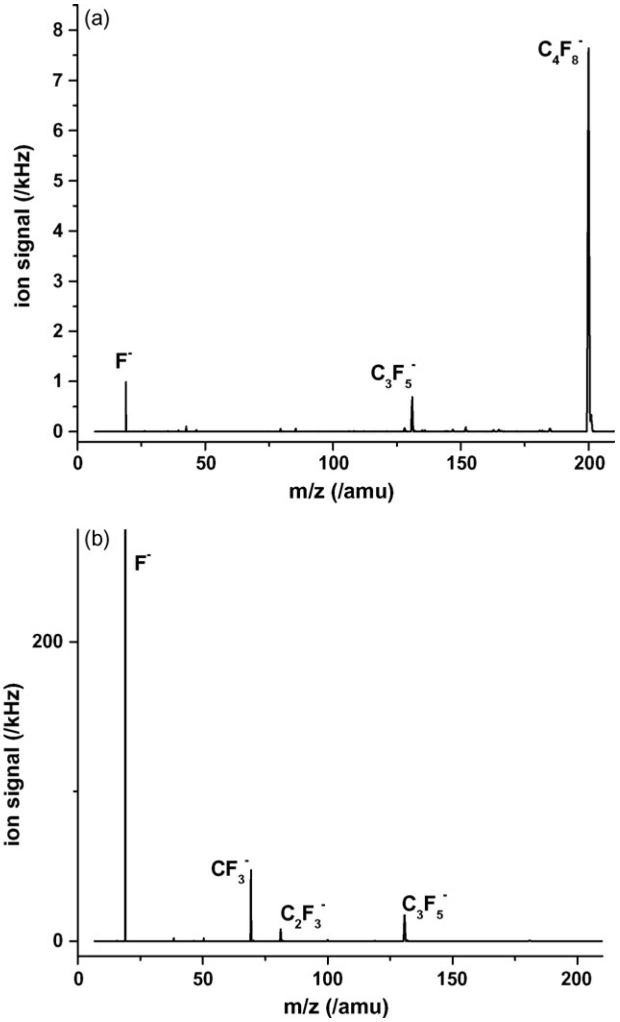


Fig. 1. Anion mass spectra of c-C_4F_8 measured at the electron energy of approximately (a) 0 eV and (b) 5.2 eV in the mass range 0–200 amu utilizing the VG-ZAB instrument.

were subsequently drawn out of the collision region by a small electrostatic field and focussed onto the entrance of a quadrupole mass spectrometer. The mass selected anions were detected by a channel electron multiplier. Details on the neutral gas pressure and electron current were recorded throughout the measurements to allow for normalization. The energy scale was calibrated by recording Cl^- from CCl_4. (The ion yield of Cl^-/CCl_4 exhibits a sharp 0 eV peak resulting from s-wave capture.) The energy scale is calibrated by the position of this peak and its full-width-at-half-maximum provides a measure for the electron energy resolution.

The second instrument we used in this study was a two sector field mass spectrometer (VG ZAB-2SEQ) of reversed Nier–Johnson type BE geometry [23]. By means of a capillary, an effusive beam of the neutral molecule enters the electron collision chamber. The energy resolution of the electron beam is low, being approximately 1 eV at an electron current of about 10 μA. This relatively high current provides us with much higher sensitivity than is available with CELIA, resulting in more anion products being observed than found in the other earlier studies. Anions formed by non-dissociative or dissociative electron attachment are extracted from the chamber by an electric field and accelerated through a potential drop of 7 kV into a mass spectrometer. They pass then through the first field free region, are momentum analyzed by a magnetic sector field B, enter a second field-free region, pass through an 81° electric sector field and are finally detected by a secondary electron multiplier. The electron energy scale of the sector field mass spectrometer is calibrated with the main resonance of NO_2^- at 4.2 eV resulting from DEA to a residual of 1,4 dinitrobenzene present in the chamber. This is required, because there is insufficient electron current close to 0 eV in this sector instrument to permit calibration using either SF_6 or CCl_4.

The use of the VG-ZAB instrument complemented the investigations made with the first instrument. Factors which favour the use of the VG-ZAB compared to CELIA include the following. Firstly, the VG-ZAB can be used to obtain estimates of electron detachment rates and can be used to investigate unimolecular decay. Secondly, and more importantly for this current investigation, in comparison to quadrupole instruments, the transmission through a sector field MS is completely mass independent, which allows for a better determination of the relative dissociative electron attachment

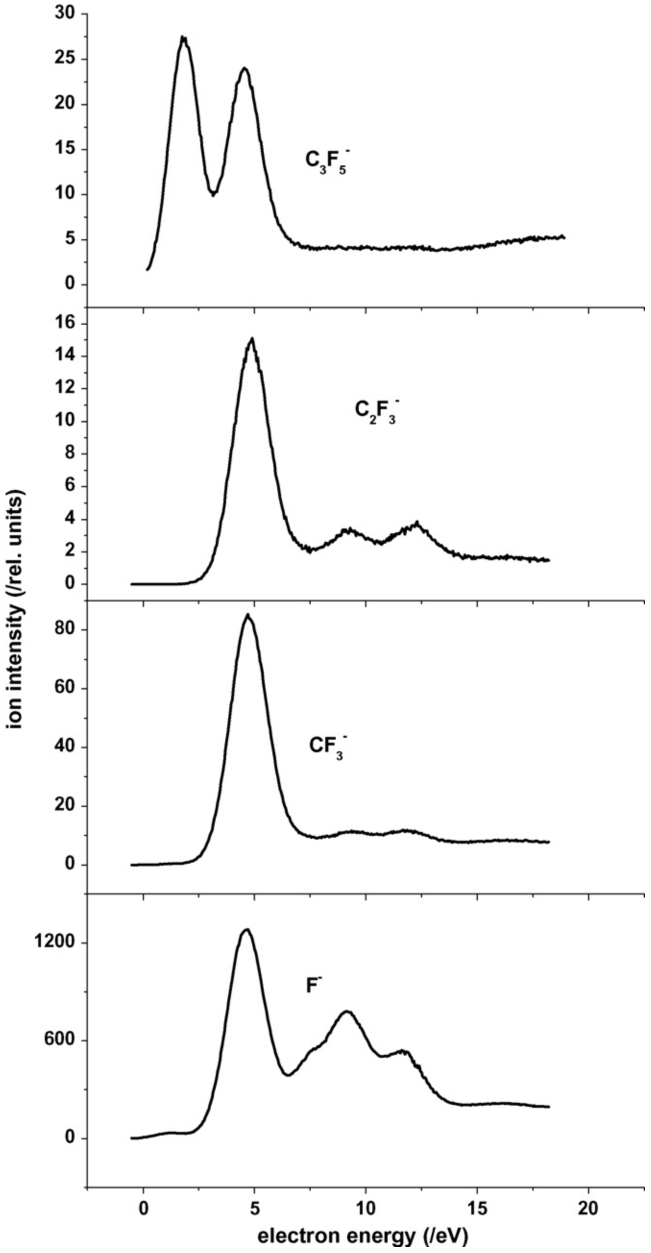


Fig. 2. Dissociative electron attachment resonances for c-C_4F_8 as a function of electron energy recorded on the VG-ZAB instrument.

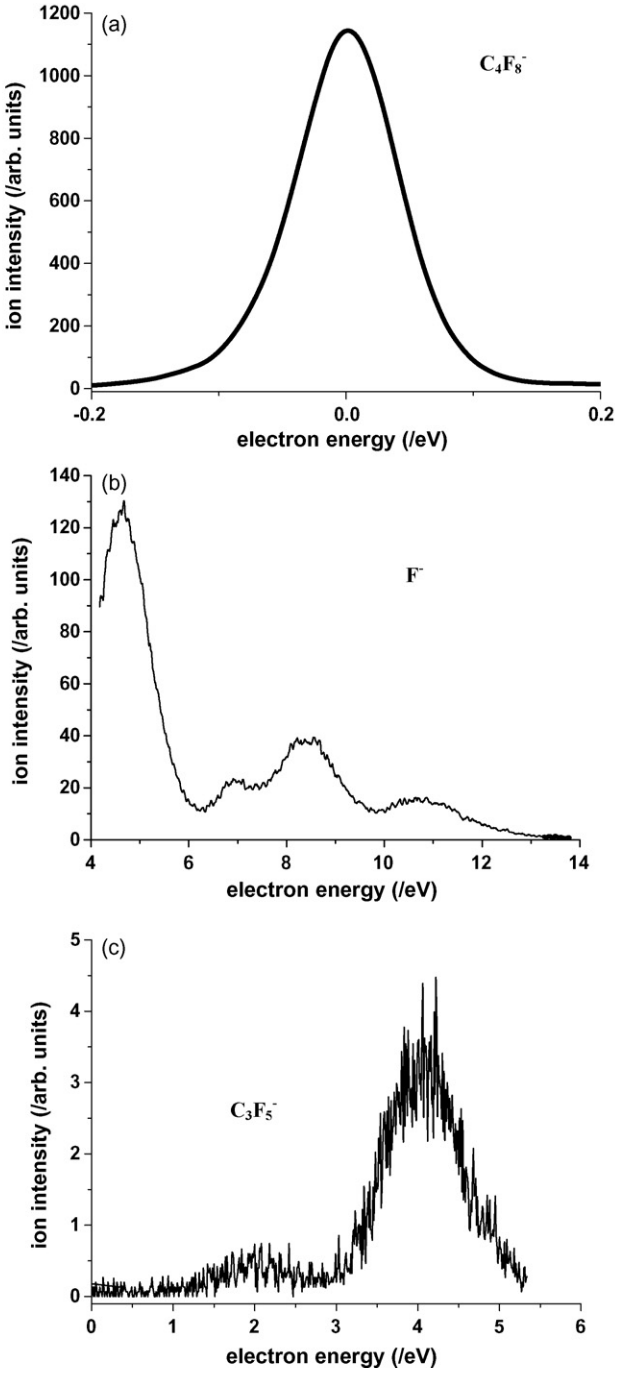


Fig. 3. Electron attachment resonances for *c*-C_4F_8 for the formation of (a) the parent anion, (b) F^- and (c) $C_3F_5^-$ measured using the CELIA instrument.

Table 1

Anion products observed, peak positions and relative intensities (peak heights) for electron attachment to *c*-C_4F_8, obtained from the current electron beam studies, compared with results obtained by Sauers et al.

Anion	Peak position [eV]	Relative intensities	
		Present results	Sauers et al.
c-$C_4F_8^-$	0	1000	1000
$C_4F_6^-$	0	1.3	
$C_3F_5^-$	2.0	3.4	
	4.1	3.0	2.9
$C_2F_3^-$	4.9	2.0	0.93
	7.9		0.14
	9.3	0.45	
	12.3	0.50	
CF_3^-	4.8	11	5.6
	9.5	1.5	
	12.0	1.5	
F^-	4.7/4.8[a]	165	100
	6.9/6.5[a]	54	36
	8.2/7.9[a]	100	64
	10.6/10.2[a]	70	42

This table presents the relative intensities obtained using the VG-ZAB data.

[a] From Sauers et al. corresponding to the same resonance with slightly different peak position being given.

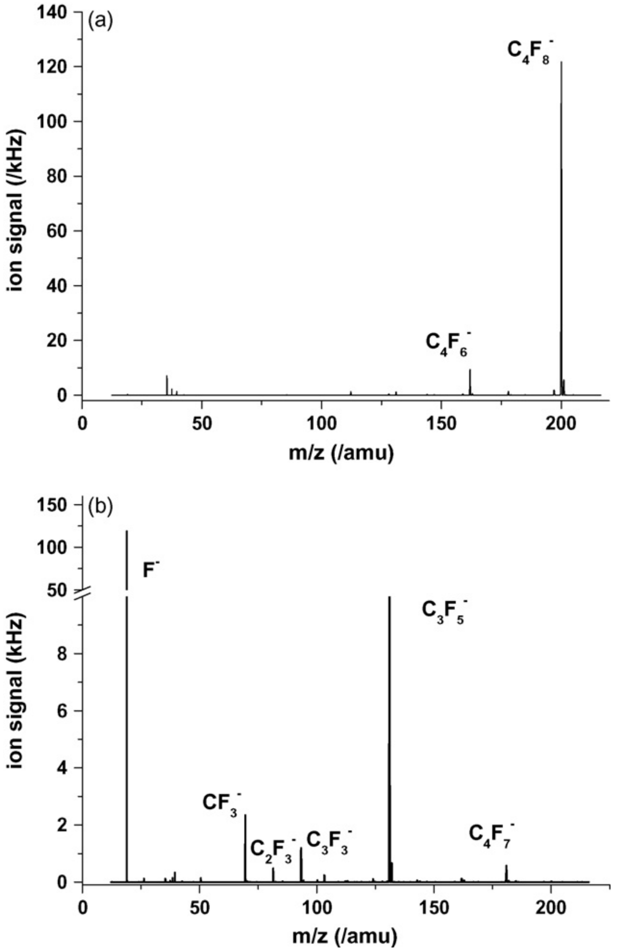


Fig. 4. Anion mass spectra of 2-C_4F_8 measured at the electron energy of approximately (a) 0 eV and (b) 4 eV in the mass range 0–200 amu utilizing the VG-ZAB instrument.

cross-sections. Thirdly, the kinetic energies of fragment anions are less critical in this instrument, because strong extraction fields are applied, and hence fewer energetic anion fragments are lost before their detection. Fourthly, the sensitivity of the VG-ZAB is higher. However, all cross-sections below 4 eV are affected strongly by the still increasing electron current that is regulated at the VG-ZAB instrument to 10 μA. In addition the poor electron energy resolution of the instrument suppresses all narrow resonances strongly. Therefore, CELIA is the best instrument to investigate energy resonances in the electron energy range of approximately 0–4 eV and to observe the narrow resonances (particularly at 0 eV for which, in any case, the VG-ZAB has insufficient electron current close to 0 eV).

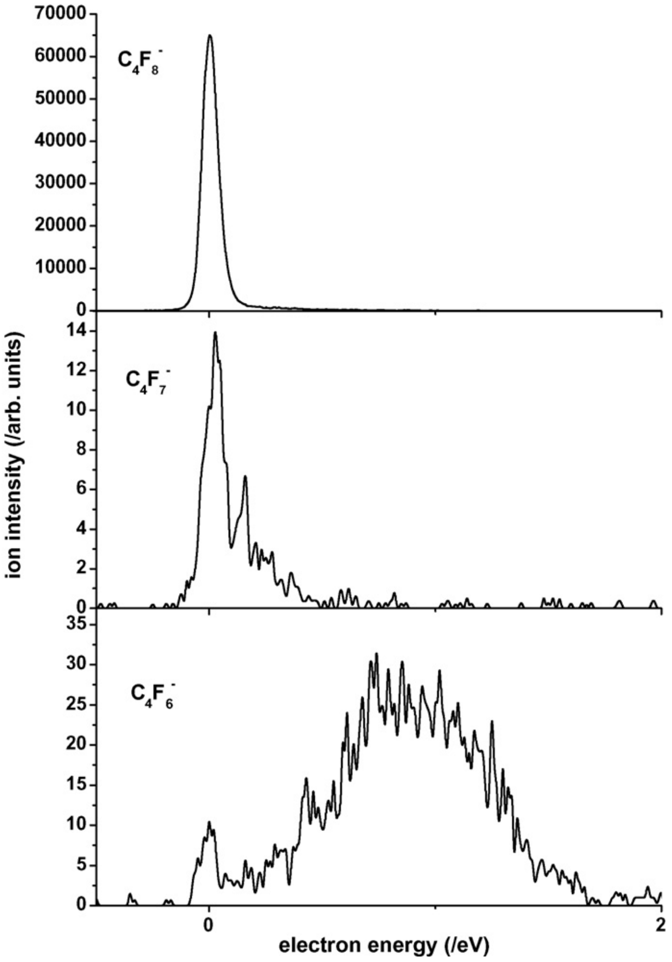


Fig. 5. Electron attachment resonances for 2-C_4F_8 for the formation of the parent anion, $C_4F_7^-$ and $C_4F_6^-$ measured using the CELIA instrument.

Thus, in conclusion, the use of these two instruments provides a very comprehensive study of electron capture to molecules.

As mentioned above the VG-ZAB can be used to determine electron detachment lifetimes. These measurements are achieved in the following way. The magnetic and the electric sectors are set to select the parent anion only. Approximately in the middle of the third field free region, between the electric sector and the detector, all of the parent anions are deflected away from the detector via a high electric field. Any electron detachment that occurs between the end of the electric sector and the deflection region results in a fast moving neutral molecule which will continue moving through the deflection region towards the detector. These fast neutral species are then detected by a channel electron multiplier at the end of the straight section. Knowing the time that the anions are in the third field free region before deflection occurs and the length of that region where electron detachment is occurring, a lifetime for the anions that decay in that time window can be determined based on the ratio of anion to neutral molecules intensities. Given that parent anions are formed with a broad range of internal energies, then the more internally excited anions will decay more rapidly than the less internally excited anions. Thus in every experiment only those anions will decay that have an appropriate range of excess internal energies that fit to the time window of the experiment. By applying different accelerating voltages different time windows are accessed and an inverse time dependence of the lifetimes and not a single decay rate is determined. A recent article describes similar types of measurements for sulfur hexafluoride relating to the electron detachment lifetime as a function of storage time in a storage ring [24]. In that work a non-exponential decay with an approximate $t^{-1.5}$ power-law dependence is found for unimolecular electron emission.

Data were recorded using the two different measurement techniques, which are routinely adopted in electron attachment studies: (i) anion mass spectra were recorded for fixed electron energies (normally at about 0 eV and at a higher energy attachment resonance) and (ii) the mass spectrometer is set to a certain anion m/z and the corresponding anion yield is recorded as a function of electron energy (0–20 eV), with the scans being normalized to gas pressures and electron beam intensity. Both of these types of scans are presented for each of the four molecules studied in the next section of this paper.

Finally, we note that the PFC gases were commercially purchased, and were used without further purification.

3. Results

3.1. c-C_4F_8

Using the VG-ZAB instrument, the anion mass spectra resulting from electron attachment to c-C_4F_8 have been recorded at two different electron energies, namely 0 and 5.2 eV, in the mass range between 0 and 200 amu. These spectra are shown in Fig. 1a and b, respectively. At 0 eV, the dominant species is the parent anion (Fig. 1a), i.e. c-C_4F_8 yields a long-lived metastable parent anion at low electron energies. Other species observed in the 0 eV mass spectrum, but at much lower intensities, are F^- and $C_3F_5^-$. These are not formed at 0 eV, but they are observed in the mass spectra because of the low electron energy resolution at which the VG-ZAB operates. As the electron energy is increased, the dominant anion product becomes F^-, as illustrated in Fig. 1b. The electron

Table 2
Anion products observed, peak positions and relative intensities (peak heights) for electron attachment to 2-C_4F_8, obtained from the current electron beam study, compared with the results of Sauers et al. and by Lifshitz and Grajower

Anion	Peak position [eV]	Relative intensities		
		Present results	Sauers et al.	Lifshitz and Grajower
2-$C_4F_8^-$	0	1000	1000	1000
$C_4F_7^-$	0	0.2	10	
$C_4F_6^-$	0	0.2	0.80	
	0.9/0.7[a]	0.4	1.5	
$C_3F_5^-$	2.3	0.22	0.80	
	4.3/4.2[a]	0.23	2.3	
$C_3F_3^-$	5.2/5.1[a]	0.13	1.0	
	8.9	0.04		
	12.4	0.14		
$C_2F_3^-$	5.4	0.07	0.40	
	8.8	0.02		
	12.5	0.01		
CF_3^-	5.3	0.30	1.30	
	8.9	0.20		
	12.5	0.14		
F^-	4.3			7
	5.3/5.2[a]	6.0	26	
	9.0	2.0		
	12.2	2.5		

The present results represent relative intensities obtained using the VG-ZAB data.

[a] From Sauers et al. corresponding to the same resonance with slightly different peak position being given.

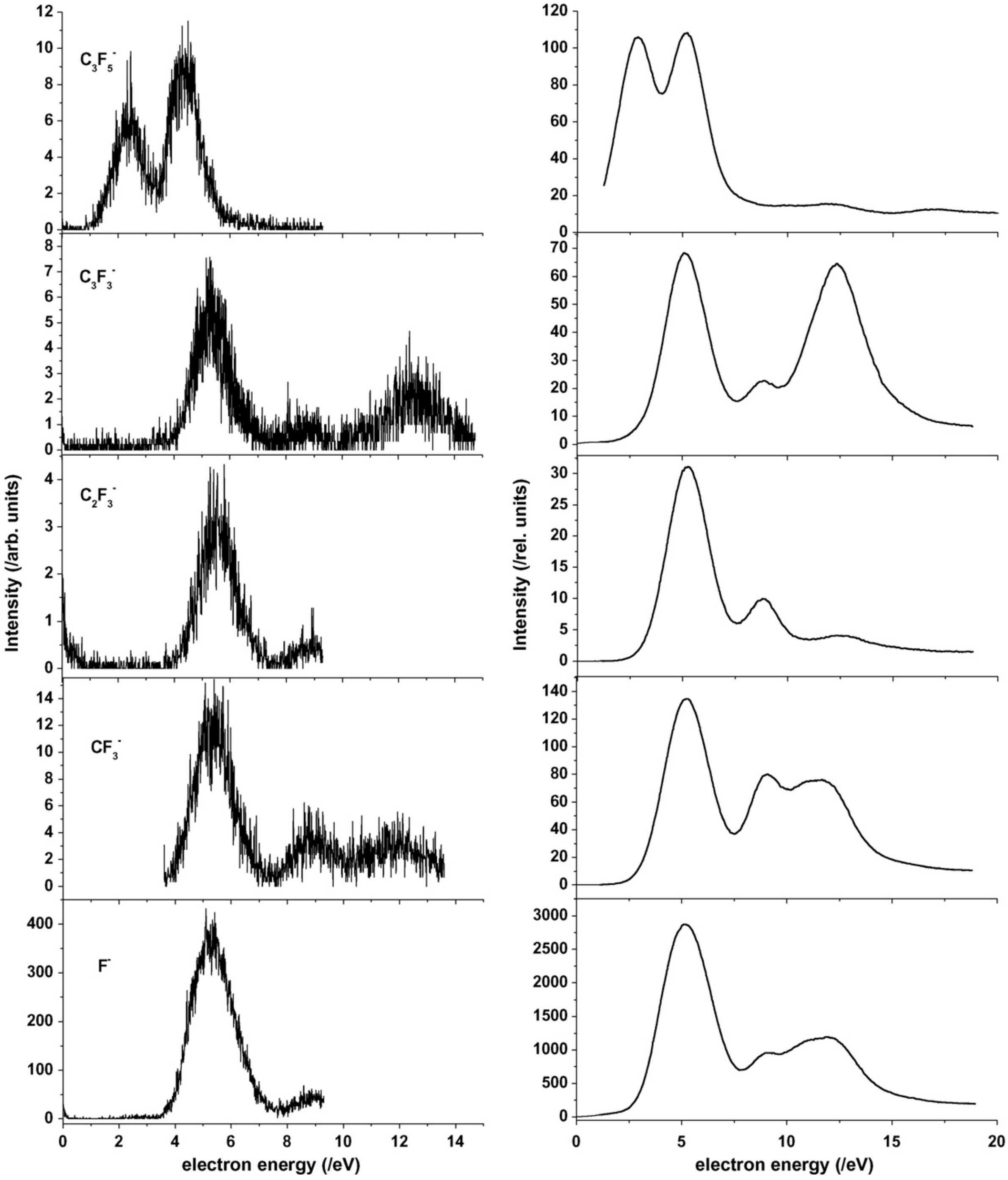


Fig. 6. Dissociative electron attachment resonances for 2-C_4F_8 recorded using CELIA (left-hand side) and the VG-ZAB (right hand side) instruments.

energy dependence of the anion products formed by dissociative electron attachment and their relative yields are shown in Fig. 2. Four product anions were observed, $C_3F_5^-$, $C_2F_3^-$, CF_3^-, and F^-.

From the CELIA measurements, the only anion observed at 0 eV is the parent (Fig. 3a). A weak resonance at 0 eV (approximately 0.1% of the parent anion signal) was observed at $m/z = 120$ amu (corresponding perhaps to $C_4F_6^-$). However, this mass was not observed with the VG-ZAB, and is therefore considered to be an impurity in the CELIA apparatus, and is therefore not shown in Fig. 3. Fig. 3b and c reproduces relative yields for the formation of F^- and $C_3F_5^-$, which are to be compared with those obtained using the VG-ZAB. These serve to illustrate that care must be taken in providing relative (or absolute) cross-sections recorded with beam apparatus. (This will be discussed further below.)

Next to the strong attachment resonance at 0 eV leading to the parent anion, F^- production is the most intense with a series of pronounced resonances being observed. The first resonance, which peaks at approximately 4.7 eV, has an intensity of about 10% of that of the parent anion signal at 0 eV. The other product anions which result from dissociative electron attachment to c-C_4F_8, namely CF_3^-, $C_2F_3^-$, and $C_3F_5^-$, are at much lower intensities than that found for the F^- channel. The anion products and the structure observed in the anion intensity versus electron energy graphs is similar to that observed by Lifshitz and Grajower [7]; we

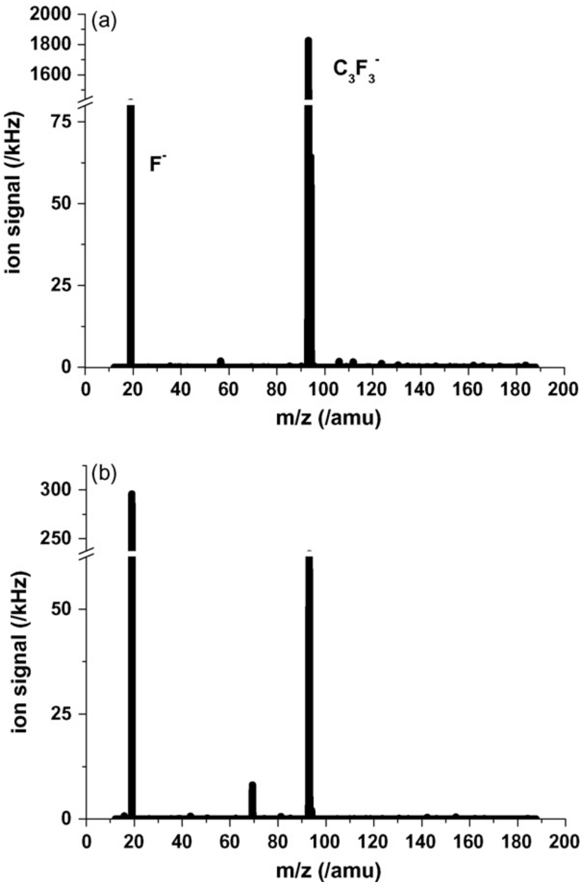


Fig. 7. Anion mass spectra of 1,3-C_4F_6 measured at the electron energy of approximately (a) 0 eV and (b) 4 eV in the mass range 0–200 amu utilizing the VG-ZAB instrument.

Table 3
Anion products observed, peak positions and relative intensities (peak heights) for electron attachment to 2-C_4F_8, obtained from the current electron beam study, compared with the results of Sauers et al.

Anion	Peak position [eV]	Relative intensities	
		Present results	Sauers et al.
$C_4F_6^-$	0	4	46
$C_3F_5^-$	0	0.5	
$C_4F_4^-$	0.8	2.2	16
	12.5	0.3	
$C_3F_4^-$	0.9	0.6	
	12.5	0.06	
$C_3F_3^-$	1.5/1.45[a]	1000	1000
	5.9		25
	7.2	72	
CF_3^-	5.8		3
F_2^-	0	0.4	
	6.6	0.3	
	12.5	1.2	
F^-	0	371[b]	
	1.6		374
	5.9/5.6[a]	165	104
	13.1	145	

The present results represent relative intensities obtained using the VG-ZAB data. Note that the intensity for the first resonance peak represents a convolution of the 0 and 1.6 eV peaks resolved in the CELIA spectrum.

[a] From Sauers et al. corresponding to the same resonance with slightly different peak position being given.

[b] This represents a superposition of the zero energy peak and the one at 1.6 eV

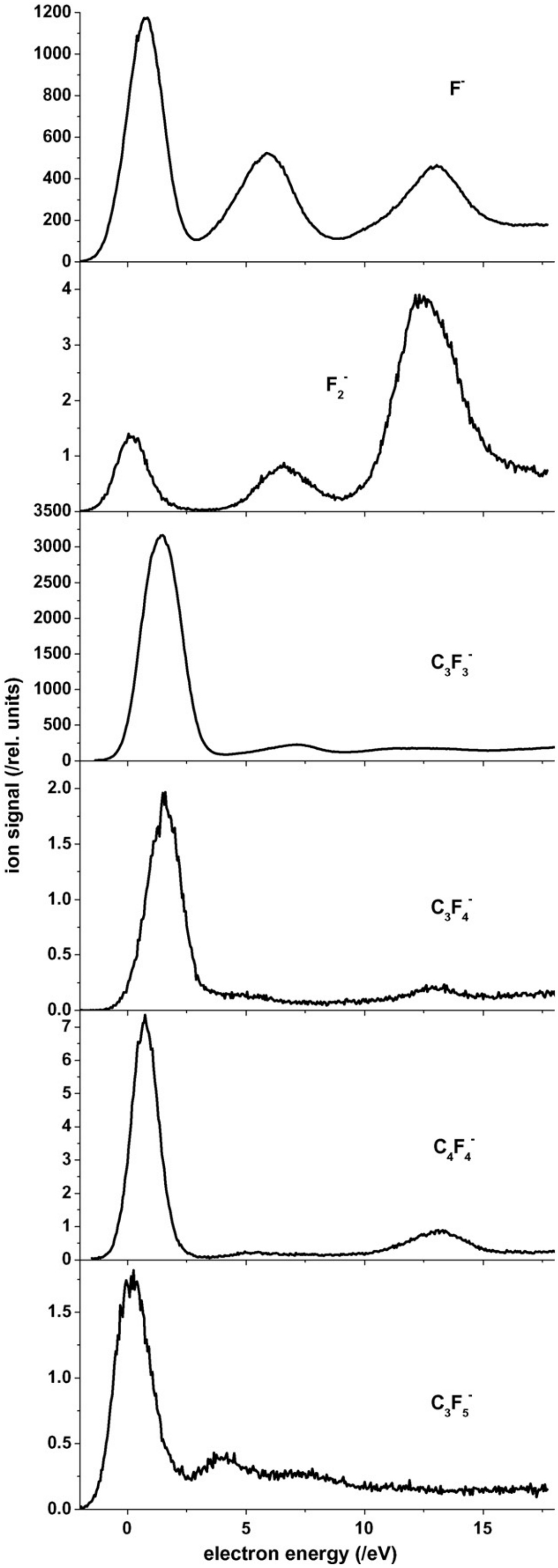
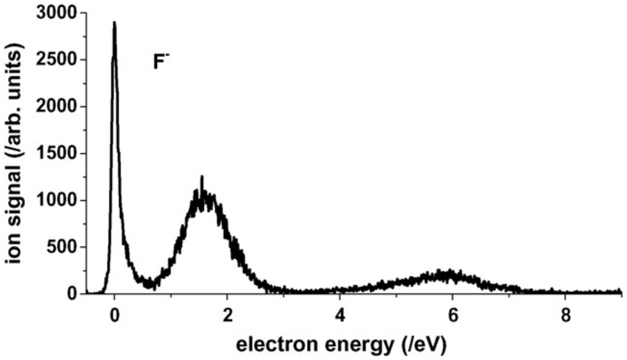


Fig. 8. Dissociative electron attachment resonances for 1,3-C_4F_6 as a function of electron energy recorded on the VG-ZAB instrument.



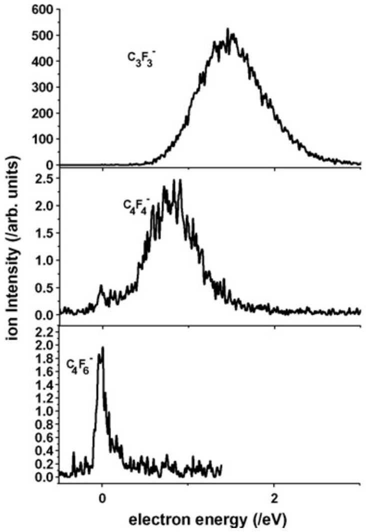


Fig. 9. Low energy (<2 eV) dissociative electron attachment resonances for 1,3-C_4F_6 as a function of electron energy recorded on the CELIA instrument.

Table 4
Anion products observed, peak positions and relative intensities (peak heights) for electron attachment to *c*-C_5F_8, obtained from the current electron beam study, compared with the results of Fenzlaff and Illenberger

Anion	Peak position [eV]	Relative intensities	
		Present results	Fenzlaff and Illenberger
c-$C_5F_8^-$	0	1000	1000
$C_5F_7^-$	2.3	0.04	0.5
	5.0	0.04	0.06
	6.9		2
	7.9	0.9	
	8.9		0.1
$C_4F_7^-$	0	0.1	
$C_4F_6^-$	0	0.2	
	0.2	0.16	
$C_4F_5^-$	3.3	0.04	
	9.2	0.03	
$C_3F_4^-$	0.5	0.04	
$C_3F_3^-$	3.3	0.04	
	7.0	0.3	
	9.9	0.2	
	13	0.1	
$C_2F_3^-$	10	0.02	
CF_3^-	7.0	0.03	
	10	0.04	
F^-	2.7	7	8.5
	6.3	6	10
	8.9	7	8.5

The present results represent relative intensities obtained using the VG-ZAB data.

do however observe for the first time some additional weak structure above 6 eV for both the product anions CF_3^- and $C_2F_3^-$. In good agreement with Lifshitz and Grajower we observe two resonances associated with the production of $C_3F_5^-$, peaking at electron energies of approximately 1.8 and 4.6 eV. We have already mentioned earlier that the lower energy peak is undetected in the other measurements. The reason for this must be associated with discrimination in the instruments which have been used to obtain the earlier spectra. In Fig. 3c the CELIA measurement at 131 amu, corresponding to the product anion $C_3F_5^-$, is presented. It can be seen that the intensity of the first peak is dramatically less than that of the second, higher energy, resonance. As mentioned earlier, CELIA is essentially field free in the ion source. This means that if sufficient kinetic energy is imparted to the fragment anions, this can lead to their loss in the instrument prior to detection; there is a strong discrimination against fragment ions produced with excess translational energy. In contrast, the VG-ZAB instrument does not suffer as much from this kinetic energy discrimination, and therefore the signals obtained using this instrument are considered to be a better representation of the relative cross-sections. This is highlighted further for the F^- anion. Fig. 3b shows that the intensities obtained for the resonance peaks observed above 6 eV recorded using CELIA are significantly reduced in intensity relative to the first resonance peak in comparison to those obtained using the VG-ZAB (Fig. 2).

Of the results presented in the literature to date, the most detailed and systematic measurements of the relative cross-sections for the production of the various anion products resulting from electron attachment to *c*-C_4F_8 as a function of electron energy have been presented by Sauers et al. [9], and our results, with the exception of a lack of the resonance in Sauers et al. paper at approximately 2.0 eV for the production of $C_3F_5^-$, agree extremely well theirs. The only other slight difference is that we have observed weak resonances at 9.5 and 12.0 eV for the production of CF_3^-. The product anions, their peak positions of the resonances and their relative intensities, compared to those obtained by Sauers et al. are presented in Table 1.

3.2. 2-C_4F_8

In agreement with the earlier studies of Lifshitz and Grajower [7] and by Sauers et al. [9], 0 eV electron attachment is dominated by formation of the parent anion. This is represented in Fig. 4a, which shows the mass spectrum taken at approximately 0 eV using the VG-ZAB instrument. The peak corresponding to $C_4F_6^-$ indicated in the figure is a result of the poor energy resolution, corresponding to electron attachment at a higher electron energy. That non-dissociative electron attachment dominates at 0 eV is further confirmed in the CELIA data. Fig. 5 shows the low energy resonances (<2 eV) for non-dissociative and dissociative electron attachment obtained using that instrument. Other than the parent anion, the only other anion to be observed with a resonance at 0 eV is $C_4F_7^-$, and, in agreement with the previous two studies, the cross-section for this channel is extremely small. The peak of the resonance for the production $C_4F_6^-$ occurs at approximately 0.9 eV. The low intensity peak observed at 0 eV, and shown in the figure, is not to be trusted, and is we believe a result of "Trojan" electrons, which are electrons produced as a result of detachment from the parent anion in the accelerating region resulting in high energy electrons [25]. These higher energy electrons can than attach to the molecules in the neutral beam causing a spurious peak at 0 eV.

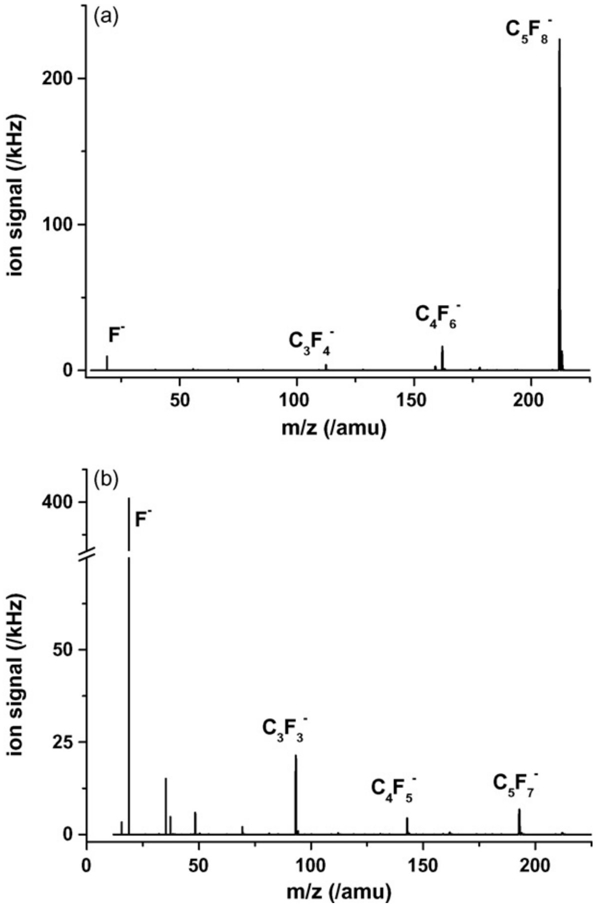


Fig. 10. Anion mass spectra of c-C_5F_8 measured at the electron energy of approximately (a) 0 eV and (b) 6 eV in the mass range 0–200 amu utilizing the VG-ZAB instrument.

As the electron energy increases more dissociative electron attachment channels are observed. This is illustrated in Fig. 4b, which shows the mass spectrum obtained using the VG-ZAB instrument for an electron energy of 4 eV. Scans of the dissociative electron attachment channels as a function of electron energy, recorded using CELIA and the VG-ZAB, are illustrated in Fig. 6. F^- is the dominant anion fragment channel, with the first resonance peaking at approximately 5.3 eV with an intensity which is only about 0.1% of that corresponding to the parent anion at 0 eV. Other dissociative electron channels are negligible in intensity by comparison. Fig. 6 serves to illustrate once again, the difficulties in determining relative cross-sections using beam apparatus for which there is significant kinetic energy discrimination. This present study is in good agreement with that presented by Sauers et al., although we have extended the electron impact energy above 8 eV up to approximately 20 eV.

Table 2 summarises the results obtained with the anion products observed, peak positions and relative intensities (peak heights) for electron attachment to 2-C_4F_8, compared with the results of Sauers et al. and by Lifshitz and Grajower.

3.3. 1,3 C_4F_6

In agreement with the results of Sauers et al. [9], we only observe a very weak resonance at 0 eV corresponding to the formation of the parent anion. The parent anion was not observed by Süzer et al., possibly because of its short lifetime [15]. In agreement with the previous two earlier works, we find that the dominant attachment process is dissociative, and this is illustrated in Fig. 7a and b. The scans, illustrating anion intensity as a function of electron impact energy, are shown in Fig. 8. These were all obtained using the VG-ZAB, and hence have been recorded at low resolution. For the more intense product anions it was possible to investigate the energy dependence under improved energy resolution on CELIA (Fig. 9). This shows that the first F^- resonance peak presented in Fig. 8 is in fact the superposition of two peaks, corresponding to a relatively sharp 0 eV and a broader 1.6 eV resonances. Scans for the other intense resonances confirmed only one resonance at electron energies below 3 eV for $C_3F_3^-$ and $C_4F_4^-$.

Table 3 presents the details on the product anions observed for electron attachment to 1,3 C_4F_6. The positions of the peaks

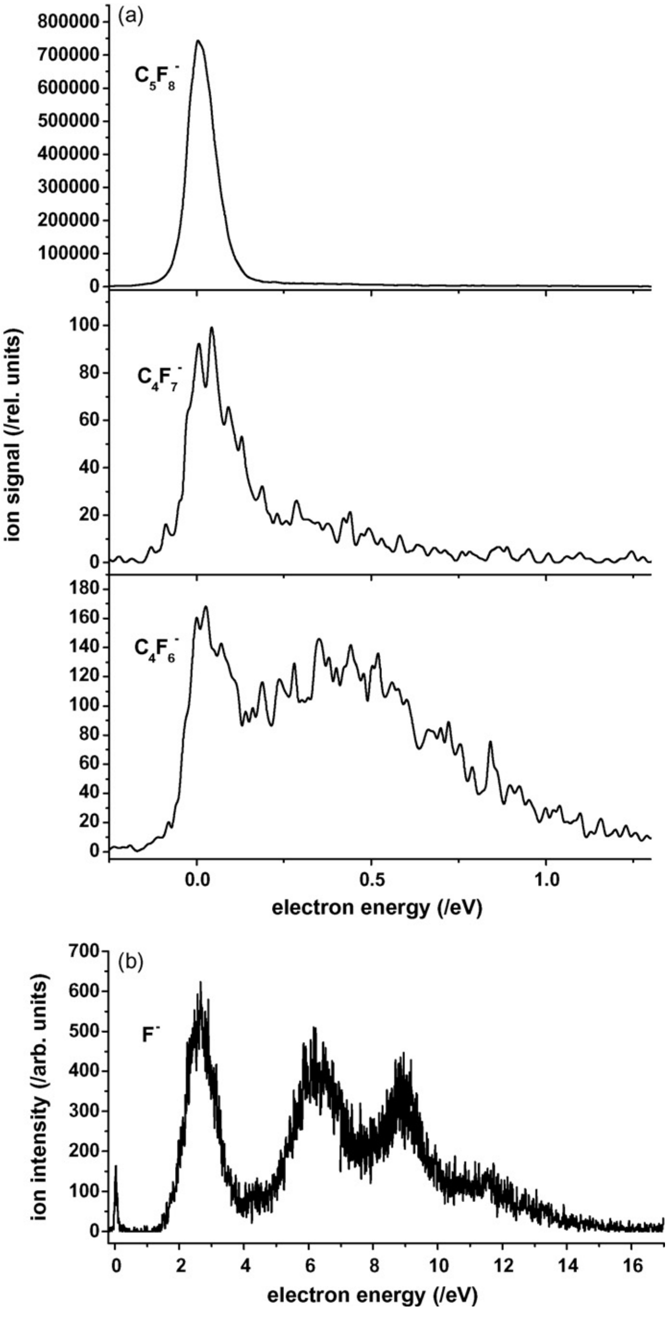


Fig. 11. (a) Low energy (<1 eV) dissociative electron attachment resonances for c-C_5F_8 as a function of electron energy recorded and (b) F^- resonances over the electron energy range 0–16 eV recorded using the CELIA instrument.

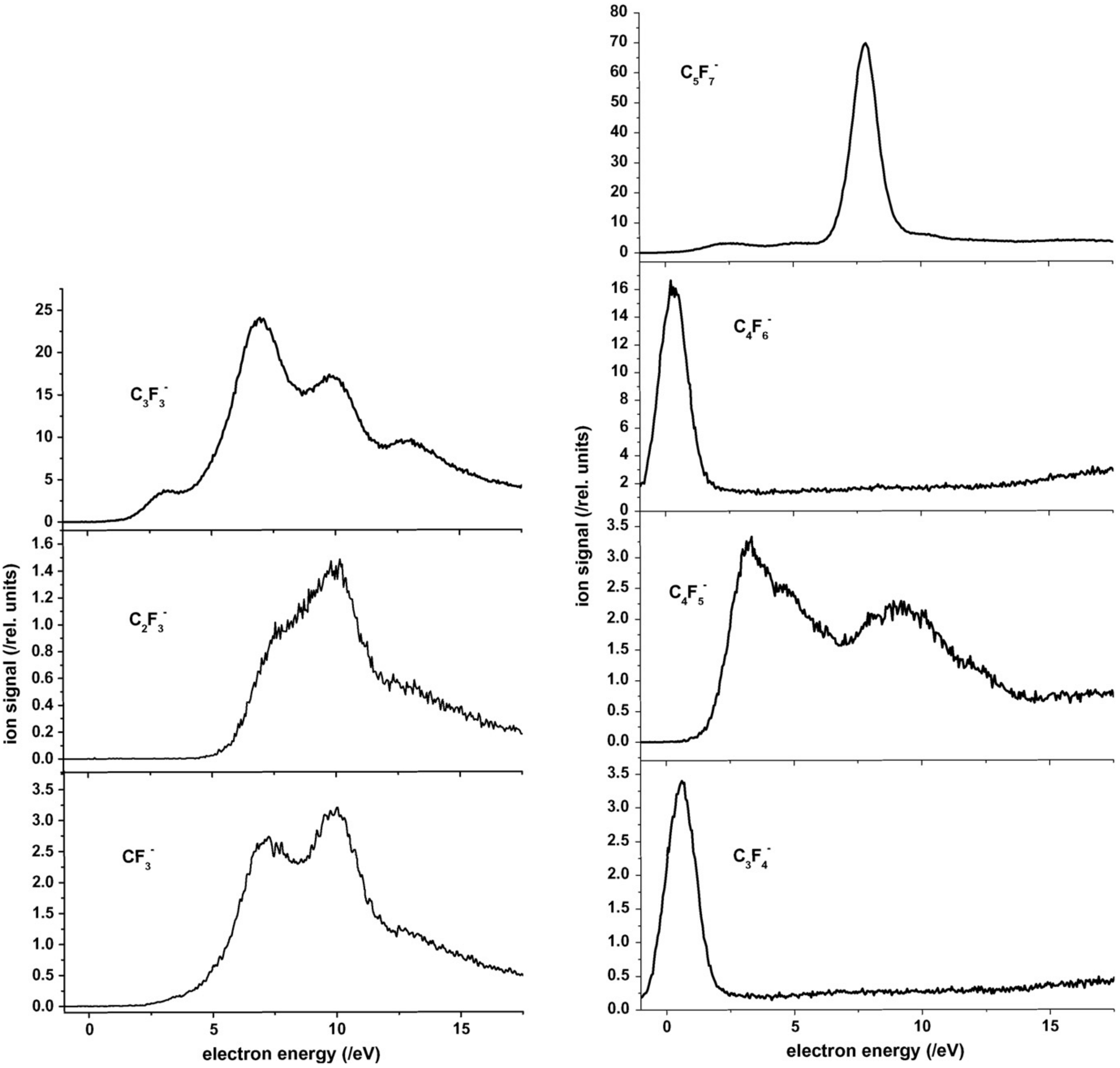


Fig. 12. Dissociative electron attachment resonances for c-C_5F_8 as a function of electron energy recorded on the VG-ZAB instrument.

for the resonances and their relative intensities compared to the measurements of Sauers et al., are presented. It can be seen that the agreement with Sauers et al. is good, although there are some discrepancies with the relative intensities. In the work by Süzer et al. [15], anion yield curves as a function of electron energy are not provided. Rather, graphs are produced to illustrate relative anion intensities at three different electron energies (0, 1 and 2 eV), so that direct quantative comparisons with our results can not be easily made. However, qualitatively there is some good agreement in that the anion $C_3F_3^-$ is the dominant product anion resulting from dissociative electron attachment. There are a number of differences of note between our investigations and those presented by Süzer et al., most notably we observe a 0 eV resonance for the formation of F^-, which is absent in the ion mass spectra presented by Süzer et al.

Table 5
Measured autodetachment lifetime for three of the four PFCs obtained at different accelerating voltages using the VG-ZAB instrument

Acceleration voltage (kV)	Lifetime [µs]		
	c-C_4F_8	2-C_4F_8	c-C_5F_8
2	120.5	138.6	122.8
3	87.0	77.9	81.7
4	66.1	53.9	66.6
5	65.9	53.6	56.6
6	52.9	46.3	52.8
7	48.0	47.1	45.4

The uncertainty associated with the lifetime values shown is never larger than ±4 µs.

3.4. c-C_5F_8

In their study, Imai and Tachibana [17] showed that the dominant fragment species observed resulting from electron attachment to c-C_5F_8 is F^-. A figure is provided in their paper of intensity of signal as a function of electron energy over the energy range 0–10 eV, which shows three resonance peaks at 2.1, 6.3 and 9.2 eV. The positions of these three peaks are in good agreement with the values we have obtained (see Table 4). However, as can be seen from Table 4, our spectra are dominated by the cross-section for parent anion formation. F^- only dominates the spectra at higher electron energies, and then its cross-section is significantly much less than that for the formation of the parent anion by low energy electrons. Fig. 10 shows anion mass spectra at two different electron energies (~0 and 6 eV) obtained using the sector field instrument. These clearly demonstrate the statements above. For 0 eV the dominant anion is the parent, whereas at an electron energy of 6 eV only fragment anions are observed, with F^- being the dominant species, i.e. no stable parent anion is observed. The relative anion yields as a function of electron energy are shown in Figs. 11 and 12, representing data from CELIA and the VG-ZAB, respectively. The parent anion was only recorded using CELIA, because of the low electron current at 0 eV for the sector instrument. Of note, the figure obtained from the CELIA data showing the electron energy resonance for the formation of $C_4F_6{}^-$ shows a double peak close to 0 eV. The peak positions of all resonances and their relative intensities, compared to earlier results presented by Fenzlaff and Illenberger [21], are summarised in Table 4. There is reasonable agreement in the peak positions with the exception of the strongest resonance leading to the $C_5F_7{}^-$ product anion.

3.5. Electron detachment lifetimes

Additional information on the electron attaching properties of the molecules has been obtained in the form of measurements of the electron detachment lifetimes for the parent anions:

$$e^- + ABC \rightarrow (ABC)^{-*} \xrightarrow{\tau} e^- + ABC \tag{2}$$

These have been obtained using the VG-ZAB at various accelerating voltages. The results of the measurements are summarized in Table 5. Note that there results have only been obtained for the parent anions for c-C_4F_8, 2-C_4F_8, and c-C_5F_8. It was not possible to measure the electron detachment lifetimes for 1,3 C_4F_6, because the intensity of the signal of the associated parent anion close to 0 eV was found to be about two orders of magnitude less than those for the other three molecules.

4. Discussion

Using mass spectrometric detection of the product anions, we have measured relative energy-dependent yields for anions resulting from non-dissociative and dissociative electron attachment to four PFCs; c-C_4F_8, 2-C_4F_8, 1,3 C_4F_6, and c-C_5F_8. Pronounced resonance profiles caused by resonant electron attachment processes (non-dissociative and dissociative) have been observed. In terms of energy positions, shapes and widths of the electron attachment peaks, the present data are in good overall agreement with results of earlier studies. Although the molecules in this study have been investigated before, there are sufficient differences in the spectra to have warranted the reinvestigation; additional product anions have been observed for the first time, inconsistencies have been resolved, and better relative cross-sections have been obtained. Many of the peak positions of the resonances observed in this investigation for the various product anions resulting from DEA to a particular PFC are at similar electron energies (at least within experimental error). Therefore, we may conclude from this that the resonances share a common precursor state of the transient parent anion.

An important conclusion coming from this study, which used two independent instruments to investigate electron attachment to a series of PFCs, is that considerable care must be taken when using beam data to determine cross-sections (relative or absolute) for electron attachment when there is little extraction voltage. Anions produced with a kinetic energy may not reach the detector, which results in a reduced peak height for a resonance at a given electron energy. Nevertheless, such data do provide important information on where resonances lie, and a reasonable indication of whether they are significant and could therefore contribute to the chemical and physical environment of technological plasmas. The difficulty associated with transmission of anions with differing kinetic energies has been used in this paper to explain discrepancies in earlier measurements, where for example some resonances were not observed.

In conclusion, we have used electron beam measurements in a classical way, extending our knowledge of the electron attachment energy resonances associated with the PFCs c-C_4F_8, 2-C_4F_8, 1,3 C_4F_6, and c-C_5F_8.

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