ELECTRON ATTACHMENT TO PERFLUOROMETHYLCYCLOHEXANE ($c\text{-}C_7F_{14}$) AND PERFLUORO-1-HEPTENE ($1\text{-}C_7F_{14}$) *

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The results of a swarm study on the attachment of slow ($\lesssim 3$ eV) electrons to $c\text{-}C_7F_{14}$ and $1\text{-}C_7F_{14}$ are presented and discussed. For both molecules the attachment cross sections show resonance maxima at 0.07 and 0.25 eV, and they are much larger for the cyclic isomer. The thermal values of the electron attachment rate are 18.3 and 1.33×10^8 s^{-1} $torr^{-1}$ for $c\text{-}C_7F_{14}$ and $1\text{-}C_7F_{14}$, respectively.

1. Introduction

The study of the electron attaching properties of halocarbon molecules is both of basic and applied significance. Knowledge of the rates and cross sections for production of parent and fragment negative ions, of the autodetachment lifetimes of metastable parent and fragment negative ions and of their energy dependences is necessary for the development of an understanding of the formation and fragmentation of molecular negative ions in impacts with low-energy electrons [1,2]. Certain halocarbons are of special significance to the environment [2] and also to other applied areas such as gaseous dielectrics (e.g., see refs. [3–5]).

In this paper we report and briefly discuss the results of a swarm study on electron attachment to $c\text{-}C_7F_{14}$ (perfluoromethylcyclohexane) and $1\text{-}C_7F_{14}$ (perfluoro-1-heptene). Although $c\text{-}C_7F_{14}$ has been the subject of earlier studies [6–14] (mostly at thermal energies), to our knowledge no study of $1\text{-}C_7F_{14}$ has been made. Recent work on electron attachment to other perfluorocarbon molecules can be found in refs. [15,16].

2. Experimental

The experimental and analytical methods used in the present study have been described previously (see, for example, refs. [1,15,17]). The purity of $c\text{-}C_7F_{14}$ and $1\text{-}C_7F_{14}$ was >97+%, and the measurements were performed at ≈298 K.

3. Results and discussion

The attachment rates, αw (α is the electron attachment coefficient, and w is the electron swarm drift velocity) [1] for $c\text{-}C_7F_{14}$ and $1\text{-}C_7F_{14}$ have been measured as a function of the pressure-reduced electric field, E/P_{298}, in mixtures with the "carrier" gases [1] N_2 and Ar at total pressures 500, 1000, 1500 and 2000 torr and 500, 1000 and 1500 torr, respectively. The perfluorocarbon pressures ranged from 5.4 to 19×10^{-5} torr for $c\text{-}C_7F_{14}$ and from 30.7 to 98.8×10^{-5} torr for $1\text{-}C_7F_{14}$. Twenty independent measurements of the attachment rate as a function of E/P_{298} have been made for $c\text{-}C_7F_{14}$ and $1\text{-}C_7F_{14}$ in mixtures

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with N_2. The average of these is listed in table 1 and is plotted in fig. 1 (solid points). Similarly, nine independent measurements of $\alpha w(E/P)$ have been made for 1-C_7F_{14} and twelve for c-C_7F_{14} using Ar as the carrier gas. The average of these is listed in table 2 and is plotted in fig. 1 (open points). In fig. 1 αw is plotted as a function of the mean electron energy $\langle\epsilon\rangle$; the relationship between $\langle\epsilon\rangle$ and E/P_{298} is given in tables 1 and 2 for N_2 and Ar respectively (see refs. [1,15]). A slight increase in αw with increasing total pressure was noticed for each molecule in both carrier gases, but it was not sufficiently outside of the experimental error (see tables 1 and 2) to be considered significant. For each carrier gas, at each E/P the average value of αw for each total pressure is within a standard deviation of the mean value of αw using all data (i.e., for all attaching and all carrier-gas pressures) for that particular E/P.

The $\alpha w(\langle\epsilon\rangle)$ functions show a characteristic maximum at 0.17 eV for c-C_7F_{14} and at 0.25 eV for 1-C_7F_{14}. They are much larger for the cyclic isomer.

The data on $\alpha w(\langle\epsilon\rangle)$, taken using N_2 as the carrier gas (table 1; fig. 1), were unfolded by application of the swarm unfolding technique [18]. The $\sigma_a(\epsilon)$ obtained are listed in table 3 and are plotted in fig. 2. Two resonance maxima are seen which for both molecules occur at ≈0.07 and ≈0.25 eV. Although the positions of the cross section maxima are the same for the two isomers, the magnitude and the energy dependence of $\sigma_a(\epsilon)$ are substantially different.

Earlier electron beam studies [11] on c-C_7F_{14} have shown that the most abundant negative ion is the long-lived metastable parent ion c-$C_7F_{14}^{-*}$ formed at thermal and epithermal energies with maximum intensity at ≈0.07 eV, in agreement with the present work. Other (weaker) ions such as $C_7F_{13}^-$, $C_6F_{11}^-$ and $C_5F_9^-$ were detected [11] at higher energies (≈0.3 eV). Based on this work and also on recent work on other fluorocar-

Table 1
Electron attachment rates for 1-C_7F_{14} and c-C_7F_{14} in N_2 [a]

E/P_{298} (V cm^{-1} torr^{-1})	$\langle\epsilon\rangle$ (eV)	1-C_7F_{14} [b]		c-C_7F_{14} [c]	
		αw (10^8 s^{-1} torr^{-1})	s.d./αw [d] (%)	αw (10^9 s^{-1} torr^{-1})	s.d./αw [d] (%)
0.007		1.07	6.9	1.47	5.1
0.01	0.041	1.38	7.5	1.86	4.6
0.02	0.046	1.87	6.0	2.41	3.1
0.03	0.054	2.13	6.5	2.58	3.6
0.04	0.064	2.49	6.7	2.80	3.6
0.05	0.075	2.97	7.0	3.05	2.4
0.06	0.087	3.43	7.2	3.25	3.7
0.07	0.099	3.92	7.4	3.44	3.8
0.08	0.109	4.67		3.69	
0.10	0.131	5.29	7.0	3.87	3.5
0.15	0.181	6.61	6.3	4.12	3.2
0.20	0.230	6.95	6.1	4.05	2.9
0.25	0.285	6.95	6.0	3 87	2.6
0.35	0.376	6.34	5.4	3.40	2.6
0.50	0.490	5.24	5.1	2.77	2.2
0.60	0.550	4.74	5.1	2.50	2 2
0.80	0.646	3.90	5.2	2.09	2.1
1.00	0.715	3.40		1.86	
1.20	0.764	3.02		1.65	
1.40	0.803	2.74		1.54	

a) The pressures of N_2 employed are: 500, 1000, 1500 and 2000 torr.
b) Average of twenty independent runs with 1-C_7F_{14} pressures in the range 30.7 to 98.8 × 10^{-5} torr.
c) Average of twenty independent runs with c-C_7F_{14} pressures in the range 5.4 to 19 × 10^{-5} torr.
d) Standard deviation divided by αw.

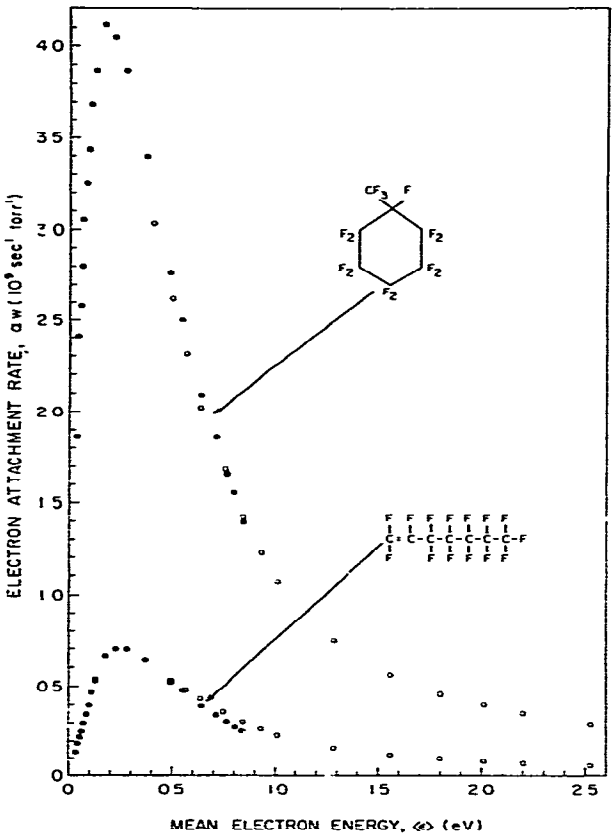


Fig. 1. Electron attachment rate as a function of mean electron energy for c-C_7F_{14} and 1-C_7F_{14}. (•) Data taken using N_2 as the carrier gas; (○) data taken using Ar as the carrier gas (see tables 1 and 2 for error estimates).

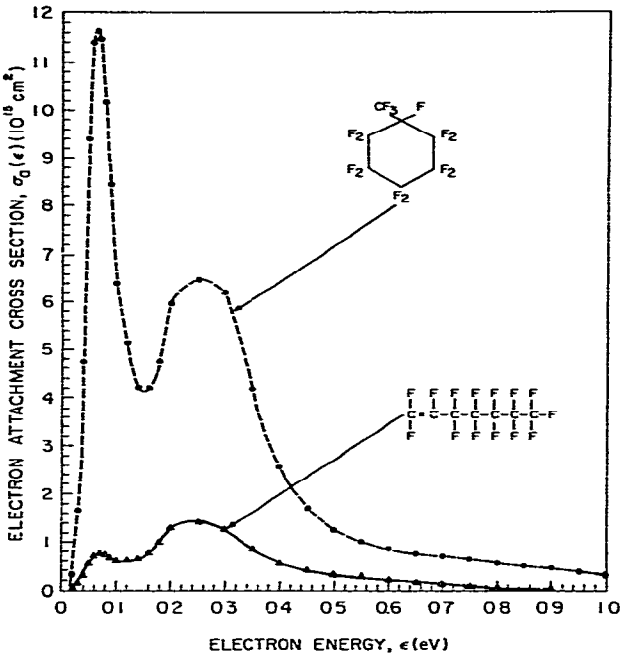


Fig. 2. Swarm-unfolded electron attachment cross sections as a function of electron energy for c-C_7F_{14} (•) and 1-C_7F_{14} (▲).

Table 2
Electron attachment rates for 1-C_7F_{14} and c-C_7F_{14} in Ar [a]

E/P_{298} (V cm^{-1} torr^{-1})	⟨ε⟩ (eV)	1-C_7F_{14} [b]		c-C_7F_{14} [c]	
		αw (10^8 s^{-1} torr^{-1})	s.d./αw [d] (%)	αw (10^9 s^{-1} torr^{-1})	s.d./αw [d] (%)
0.006	0.409	5.36	8.6	3.03	3.8
0.010	0.498	5.24	7.5	2.62	5.0
0.015	0.570	4.80	6.0	2.31	4.3
0.02	0.641	4.31	4.9	2.02	4.3
0.03	0.752	3.60	4.5	1.69	3.8
0.04	0.848	3.05	3.9	1.42	4.0
0.05	0.935	2.63	3.8	1.22	3.8
0.06	1.012	2.29	3.8	1.07	3.5
0.10	1.285	1.57	3.5	0.74	3.7
0.15	1.559	1.14	3.6	0.56	3.5
0.20	1.795	0.92	3.5	0.46	4.0
0.25	2.008	0.79	3.6	0.40	3.4
0.30	2.197	0.69	3.6	0.35	3.5
0.40	2.526	0.55	3.8	0.29	3.5
0.50	2.808	0.50	–	0.26	–

[a] The pressures of Ar employed are: 500, 1000 and 1500 torr.
[b] Average of nine independent runs with 1-C_7F_{14} pressures ranging from 35.3 to 52.1 × 10^{-5} torr.
[c] Average of twelve independent runs with c-C_7F_{14} pressures in the range 9.7 to 17.1 × 10^{-5} torr.
[d] Standard deviation divided by αw.

Table 3
Electron attachment cross sections, $\sigma_a(\epsilon)$, for 1-C_7F_{14} and c-C_7F_{14} [a]

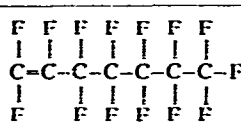
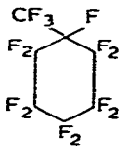
ϵ(eV)	$\sigma_a(\epsilon)$ (10^{-16} cm^2)				
	1-C_7F_{14}	c-C_7F_{14}			
0.02	0.31	3.3	0.40	5.45	25.7
0.03	1.26	16.6	0.45	4.02	16.9
0.04	3.02	47.3	0.50	3.29	12.4
0.05	5.75	93.9	0.55	2.79	10.1
0.06	7.01	113.9	0.60	2.19	8.47
0.07	7.44	114.7	0.65	1.67	7.46
0.08	7.17	101.7	0.70	1.30	7.00
0.10	5.90	63.9	0.75	0.90	6.33
0.12	6.09	51.4	0.80	0.58	5.66
0.14	6.30	42.2	0.85	0.35	4.91
0.16	7.61	42.0	0.90	0.21	4.39
0.18	9.93	47.6	0.95	0.12	3.78
0.20	12.93	59.7	1.0	0.05	2.79
0.25	14.02	64.6	1.1	0.012	1.54
0.30	8.31	62.0	1.2	0.001	0.47
0.35	12.60	42.0	1.3		0.07

[a] The major error in these cross sections is the systematic and random error of the attachment rates on which they are based. This error is ≈10% (see ref. [15]).

bon compounds [4,5], the 0.07 eV resonance in fig. 2 should be mostly due to the parent c-$C_7F_{14}^{-*}$ ion and the 0.25 eV resonance due mostly to fragment ions. Other beam studies [10,13] found the autodetachment lifetime τ_a of c-$C_7F_{14}^{-*}$ at ≈0.0 eV to be 793 μs [10] and 757 μs [13]. Although no similar work has been reported for 1-C_7F_{14}, on the basis of the work on c-C_7F_{14} and other fluorocarbons (refs. [1,4,5,10,15, 16,19]), the 1-$C_7F_{14}^{-*}$ ion is expected to form at ≈0.07 eV and to be long-lived ($\tau_a > 10^{-6}$ s); fragment negative ions would predominate at higher energies.

The results of earlier studies [8,9,12,14] on the value of the thermal (T = 298 K) attachment rate for c-C_7F_{14} are compared in table 4 with the present value of 18.3×10^8 s^{-1} torr^{-1}. The thermal value of the attachment rate for 1-C_7F_{14} is 1.33×10^8 s^{-1}

Table 4
Values of the thermal attachment rate, positions, ϵ_{max}, of the maxima in the attachment cross section $\sigma_a(\epsilon)$ and values of $\sigma_a(\epsilon)$ at ϵ_{max} for 1-C_7F_{14} and c-C_7F_{14}

Molecule	Structural formula	Thermal attachment rate [a] (10^8 s^{-1} torr^{-1})	ϵ_{max} (eV)	$\sigma_a(\epsilon_{max})$ (10^{-15} cm^2)
perfluoro-1-heptene (1-C_7F_{14})		1.33	0.07; 0.25	0.75; 1.4
perfluoromethyl-cyclohexane (c-C_7F_{14})		18.3 13 [14] 16.9 [12] 26 [9] 31.9 [8]	0.07; 0.25 0.15 [7]	11.5; 6.5 7.5 [7]

[a] Determined by integrating the $\sigma_a(\epsilon)$ obtained in this work (table 3) over a maxwellian function (T = 298 K) (ref. [19]).

$torr^{-1}$ (i.e. ≈14 times smaller than for c-C_7F_{14}).

The higher values of the attachment cross section for the cyclic perfluorocarbon are consistent with the conclusion we reached recently [15,16] that the cyclic structure increases the attachment cross section. They are also consistent with the higher dielectric strength of c-C_7F_{14} relative to 1-C_7F_{14} (refs. [3–5]). Christophorou et al. [4] reported the relative dc breakdown voltage of c-C_7F_{14}, 1-C_7F_{14} and SF_6 to be 2.2, 1.2 and 1.0, respectively.

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