

Electron attachment to perfluorocarbon compounds. II. $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} : Relevance to gaseous dielectrics^{a)}

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Electron attachment rates αw as a function of the pressure-reduced electric field have been measured for $c\text{-C}_5\text{F}_8$ (perfluorocyclopentene), $c\text{-C}_6\text{F}_{10}$ (perfluorocyclohexene), $c\text{-C}_6\text{F}_{12}$ (perfluoro-1,2-dimethylcyclobutane), C_7F_8 (perfluorotoluene), and C_8F_{16} (perfluoro-1,3-dimethylcyclohexane). The thermal values $(\alpha w)_{\text{ther}}$ of the attachment rate for these compounds are 12.8, 12.9, 5.0, 9.2, and $2.4 \times 10^9 \text{ sec}^{-1} \text{ Torr}^{-1}$, respectively. The electron attachment cross sections $\sigma_a(\epsilon)$ as functions of the electron energy ϵ have been determined using the swarm-unfolding technique; they show distinct structure at $\epsilon < 1.5 \text{ eV}$. The electron attachment properties for the perfluorocarbons (PFCs) studied in this and the preceding paper depend strongly on the molecular structure. Thus (i) open-chain saturated PFCs do not attach electrons as efficiently as the unsaturated PFCs; (ii) for saturated PFCs an increase in molecular size (chain length) increases αw ; (iii) the presence of multiple bonds in the molecule dramatically increases the magnitude of αw for the saturated open-chain PFCs, but it has only a small effect for cyclic PFCs; (iv) the cyclic nature of the PFCs seems to increase greatly $\sigma_a(\epsilon)$; and (v) for single-bonded cyclic PFCs, substitution of CF_3 groups for F atoms increases $(\alpha w)_{\text{ther}}$ more than does an increase in molecular size; in double-bonded cyclic compounds increase in ring size increases $\sigma_a(\epsilon)$ at thermal energies. The PFCs studied in this and the preceding paper have higher dielectric strengths than SF_6 . This improvement in dielectric strength can be attributed to their large $\sigma_a(\epsilon)$ over a wider energy range (to $\sim 1.5 \text{ eV}$). Their use as unitary gases and/or as additives to multicomponent gas mixtures is discussed.

I. INTRODUCTION

In the preceding paper (Part I), we discussed the electron attaching properties of perfluorinated four-carbon compounds and the significance of knowledge of the electron attachment rates and cross sections to the understanding of the interactions of these molecules with low-energy electrons. The energy dependence of the electron attachment cross sections, for example, provides information about the negative ion states of these molecules. The magnitude and energy dependence of the cross sections for formation as well as for the fragmentation and decay channels of these negative ion states provides information as to the influence of structure on the details of the electron-polyatomic molecule interaction in the extreme low-energy regime.

In this paper, we extend the study to perfluorocarbon compounds with five or more carbon atoms and discuss the relevance of the measured attachment rates and calculated cross sections as a function of electron energy ϵ to the use of these perfluorinated compounds as gaseous dielectrics. The perfluorocarbons studied in this and the preceding paper can be used both as unitary dielectric gases and/or as additives to multicomponent gas mixtures in combination with other gases which may themselves not attach electrons.¹⁻⁶ The knowledge of electron attachment cross sections can serve as a guide

to choosing appropriate components for multicomponent gas mixtures.¹⁻⁶

II. EXPERIMENTAL SECTION

The experimental and analytical techniques employed and the apparatus used to measure the electron attachment rates for the compounds studied in this paper are identical to those used and discussed in the preceding paper, and they will not be discussed further. The sources of error in our measurements have been discussed in the preceding paper and that discussion applies here as well. In Table I are listed the compounds investigated in this paper along with their structural formulas, boiling points, and range of partial pressures used. The quoted purities of these compounds, as supplied by Columbia Organic Chemical Company, are 97+%.

III. RESULTS

A. Electron attachment rates as a function of E/P and $\langle \epsilon \rangle$

In Tables II and III are listed the measured electron attachment rates as a function of E/P (the pressure-reduced electric field) for the five compounds studied using nitrogen (Table II) and argon (Table III) as the carrier gas. The mean energies $\langle \epsilon \rangle$ of the electrons in each gas as a function of E/P are listed in these tables also.

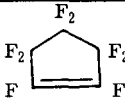
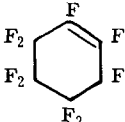
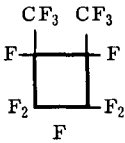
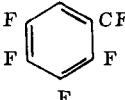
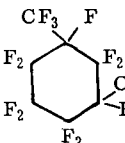
Figures 1 and 2 show, respectively, the electron attachment rates αw as a function of $\langle \epsilon \rangle$ with nitrogen and argon as the carrier gas. They are remarkably close in the range where the computed $\langle \epsilon \rangle$'s overlap. This close agreement of the electron attachment rates measured using the two carrier gases for all of the per-

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TABLE I. Nomenclature, molecular and structural formulas, pressure ranges used, and boiling and freezing points for $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} .

| Perfluorocarbon | Molecular formula | Structural formula | $P_{\text{C}_5\text{F}_8}$ in N_2 ^a (10^{-5} torr) | $P_{\text{C}_6\text{F}_{10}}$ in Ar ^b (10^{-5} torr) | Boiling point (°C) | Freezing point (°C) |
|-----------------------------------|-----------------------------|--|---|--|--|--------------------------------------|
| Perfluorocyclopentene | $c\text{-C}_5\text{F}_8$ |  | (16) ^c 4.53–43.39 | (9) 8.73–17.62 | 25 ^d 33 to 35 ^e | |
| Perfluorocyclohexene | $c\text{-C}_6\text{F}_{10}$ |  | (20) 1.0–7.73 | (2) 9.68 | 54 ^d | |
| Perfluoro-1,2-dimethylcyclobutane | $c\text{-C}_6\text{F}_{12}$ |  | (19) 3.94–9.69 | (8) 5.84–9.75 | | |
| Perfluorotoluene | C_7F_8 |  | (7) 1.46–4.83 | (1) 4.75 | 80.5 ^f 103 ^d | –98 ^f |
| Perfluoro-1,3-dimethylcyclohexane | C_8F_{16} |  | (8) 5.90–9.70 | (9) 7.88–17.49 | 100.2 ^d 101.5 ^g 102.1 ^g | –55 ^g –70 ^f |

^aThe pressures of N_2 employed are 500, 1000, 1500, and 2000 torr.^bThe pressures of Ar employed are 500, 1000, and 1500 Torr.^cThe numbers in parentheses give the number of independent runs made in N_2 or Ar.^dE. R. Larsen, *Fluorine Chem. Rev.* **3**, 1 (1969).^eT. J. Brice, *Fluorine Chemistry*, edited by J. H. Simons (Academic, New York, 1950), Vol. I, Chap. 13, p. 452.^fJ. B. Irving and D. T. Jamieson, *J. Fluorine Chem.* **5**, 449 (1975).^gJ. H. Simons and J. T. Brice, *Fluorine Chemistry*, edited by J. H. Simons (Academic, New York, 1954), Vol. II, Chap. 6, p. 405.TABLE II. Electron attachment rates for $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} in N_2 .

| E/P_{298} ($\text{V cm}^{-1} \text{ torr}^{-1}$) | $\langle \epsilon \rangle$ (eV) | αw in N_2 ($10^9 \text{ sec}^{-1} \text{ torr}^{-1}$) | | | | | $(\alpha w)_{\text{max}}^a$ ($10^9 \text{ sec}^{-1} \text{ torr}^{-1}$) |
|---|------------------------------------|---|-----------------------------|-----------------------------|------------------------|---------------------------|--|
| | | $c\text{-C}_5\text{F}_8$ | $c\text{-C}_6\text{F}_{10}$ | $c\text{-C}_6\text{F}_{12}$ | C_7F_8 | C_8F_{16} | |
| 0.02 | 0.046 | 11.62 | 11.88 | 4.73 | 8.42 | 2.49 | 13.25 |
| 0.03 | 0.054 | 10.72 | 10.81 | 4.51 | 7.71 | 2.55 | 12.55 |
| 0.04 | 0.064 | 9.46 | 9.89 | 4.33 | 7.21 | 2.65 | 11.44 |
| 0.05 | 0.075 | 8.47 | 8.91 | 4.21 | 6.76 | 2.77 | 10.60 |
| 0.06 | 0.087 | 7.58 | 7.98 | 4.08 | 6.33 | 2.85 | 9.70 |
| 0.07 | 0.099 | 6.88 | 7.28 | 3.98 | 5.91 | 2.96 | 9.05 |
| 0.10 | 0.131 | 5.47 | 5.91 | 3.79 | 5.12 | 3.12 | 7.85 |
| 0.15 | 0.181 | 4.19 | 4.58 | 3.47 | 4.15 | 3.15 | 6.60 |
| 0.20 | 0.230 | 3.42 | 3.73 | 3.16 | 3.48 | 2.96 | 5.85 |
| 0.25 | 0.285 | 2.90 | 3.17 | 2.87 | 2.98 | 2.74 | 5.30 |
| 0.35 | 0.376 | 2.23 | 2.38 | 2.38 | 2.36 | 2.33 | 4.60 |
| 0.50 | 0.490 | 1.67 | 1.73 | 1.86 | 1.80 | 1.84 | 3.97 |
| 0.60 | 0.550 | 1.48 | 1.50 | 1.64 | 1.59 | 1.63 | 3.72 |
| 0.80 | 0.646 | 1.24 | 1.19 | 1.36 | 1.31 | 1.33 | 3.40 |
| 1.00 | 0.715 | 1.09 | 1.08 | 1.20 | 1.18 | 1.18 | 3.20 |
| 1.20 | 0.764 | 0.99 | 0.91 | 1.05 | 1.08 | 1.06 | 3.08 |
| 1.40 | 0.803 | 0.90 | 0.81 | 0.96 | 1.02 | 0.97 | 3.00 |
| 1.70 | 0.846 | 0.85 | 0.68 | 0.88 | 0.95 | 0.86 | 2.93 |

^aThe values of $(\alpha w)_{\text{max}}$ were obtained using Eq. (9) of Part I and the $f_{\text{N}_2}(\epsilon, \langle \epsilon \rangle)$ functions for N_2 (see Sec. II, D, Part I).

TABLE III. Electron attachment rates for $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} in Ar.

| E/P_{298} (V cm ⁻¹ torr ⁻¹) | $\langle\epsilon\rangle$ (eV) | αw in Ar (10 ⁹ sec ⁻¹ torr ⁻¹) | | | | | $(\alpha w)_{\max}^a$ (10 ⁹ sec ⁻¹ torr ⁻¹) |
|---|----------------------------------|---|-----------------------------|-----------------------------|------------------------|---------------------------|--|
| | | $c\text{-C}_5\text{F}_8$ | $c\text{-C}_6\text{F}_{10}$ | $c\text{-C}_6\text{F}_{12}$ | C_7F_8 | C_8F_{16} | |
| 0.010 | 0.498 | 1.64 | 1.54 | 1.78 | 1.61 | 1.91 | 3.89 |
| 0.015 | 0.570 | 1.43 | 1.31 | 1.56 | 1.41 | 1.69 | 3.63 |
| 0.02 | 0.641 | 1.27 | 1.15 | 1.39 | 1.28 | 1.46 | 3.39 |
| 0.03 | 0.752 | 1.08 | 0.97 | 1.15 | 1.10 | 1.23 | 3.13 |
| 0.04 | 0.848 | 0.93 | 0.83 | 0.97 | 0.95 | 1.04 | 2.90 |
| 0.05 | 0.935 | 0.81 | 0.73 | 0.84 | 0.84 | 0.90 | 2.81 |
| 0.06 | 1.012 | 0.72 | 0.66 | 0.74 | 0.75 | 0.79 | 2.70 |
| 0.10 | 1.285 | 0.51 | 0.47 | 0.53 | 0.54 | 0.57 | 2.38 |
| 0.15 | 1.559 | 0.38 | 0.36 | 0.42 | 0.38 | 0.45 | 2.11 |
| 0.20 | 1.797 | 0.31 | 0.30 | 0.37 | 0.32 | 0.37 | 1.87 |
| 0.25 | 2.008 | 0.27 | 0.26 | 0.33 | 0.26 | 0.33 | 1.66 |
| 0.30 | 2.197 | 0.23 | 0.23 | 0.30 | 0.24 | 0.29 | 1.50 |
| 0.40 | 2.526 | 0.19 | 0.19 | 0.25 | 0.19 | 0.24 | 1.25 |
| 0.50 | 2.808 | 0.17 | 0.16 | 0.22 | 0.17 | 0.21 | 1.08 |

^aThe values of $(\alpha w)_{\max}$ were obtained using Eq. (9) of Part I and the $f_{\text{Ar}}(\epsilon, \langle\epsilon\rangle)$ functions for Ar (see Sec. III.D, Part I).

fluorocarbon compounds studied indicates that the distribution of electron energies in the overlapping mean energy range is similar for both carrier gases. It also demonstrates the consistency of the data and the mean energy scales as established by the two carrier gases (N_2 and Ar). The attachment rates were found to be independent both of the attaching and the carrier gas pressures. The lack of pressure dependence indicates that all of the ions which are formed in the collision of slow electrons with the perfluorocarbon molecules under study are stabilized at the pressures employed and that the measured attachment rates are the total electron capture rates for these compounds.

The magnitudes of the electron attachment rates for all the perfluorocarbons studied in this paper is largest at near-thermal energies and decreases with increasing $\langle\epsilon\rangle$ above thermal energy, except for C_8F_{16} for which the attachment rate has a maximum at $\langle\epsilon\rangle \approx 0.18$ eV.

B. Electron attachment cross sections as a function of ϵ

Using the swarm unfolding technique,⁷ we have calculated the electron attachment cross sections $\sigma_a(\epsilon)$ for these compounds as is discussed in Part I. These are plotted as a function of ϵ in Figs. 3 and 4 and are listed

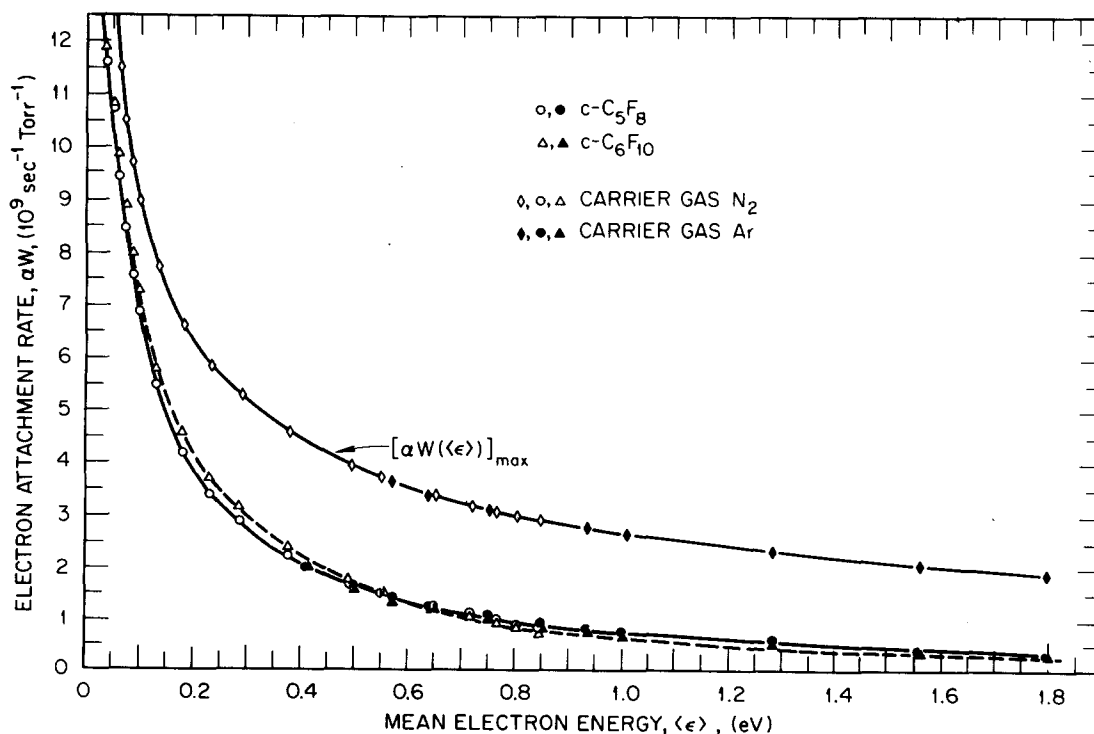


FIG. 1. Electron attachment rate αw vs $\langle\epsilon\rangle$ for $c\text{-C}_5\text{F}_8$ (○, ●) and $c\text{-C}_6\text{F}_{10}$ (△, ▲) in N_2 (open points) and in Ar (solid points).

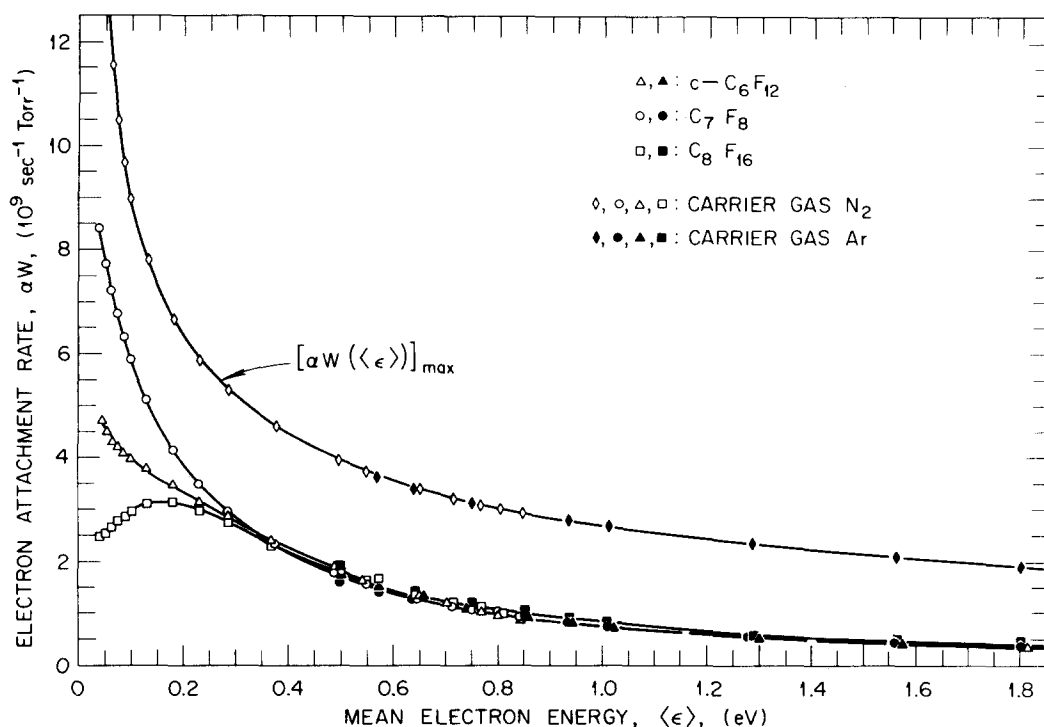


FIG. 2. Electron attachment rate αw vs $\langle \epsilon \rangle$ for $c\text{-C}_6\text{F}_{12}$ (Δ, \blacktriangle), C_7F_8 (\circ, \bullet), and C_8F_{16} (\square, \blacksquare) in N_2 (open points) and in Ar (solid points).

in Table IV. The attachment cross sections for SF_6 and the maximum cross section for s -wave capture are also plotted in each of the figures for comparison.

Several features of $\sigma_a(\epsilon)$ deserve comment (see Figs. 3 and 4 and Tables IV and V). For all the nonaromatic

perfluorocarbons, three negative ion resonances (NIR's) can be identified below ~ 1 eV. For the aromatic compound perfluorotoluene (C_7F_8), at least two NIR's are detected, and this is consistent with earlier observations by Gant and Christophorou⁸ on perfluorobenzene.

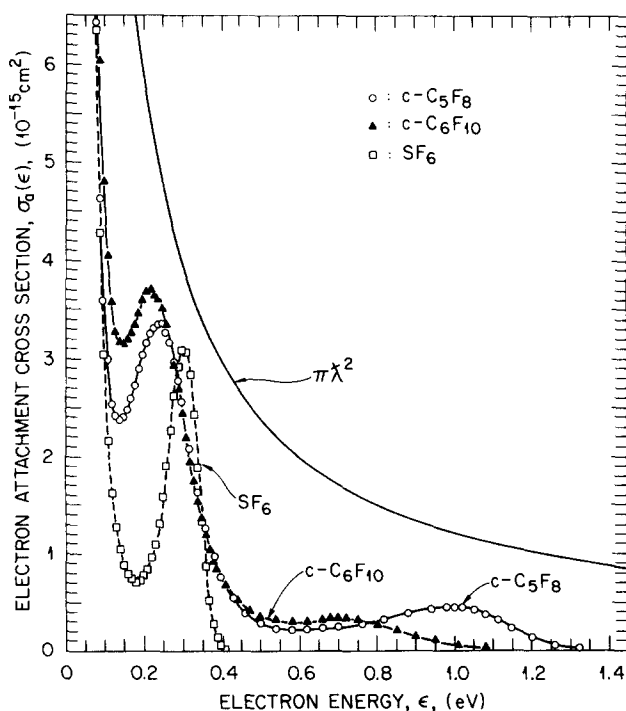


FIG. 3. Electron attachment cross section $\sigma_a(\epsilon)$ as a function of electron energy ϵ for $c\text{-C}_5\text{F}_8$ (\circ), $c\text{-C}_6\text{F}_{10}$ (\blacktriangle), and SF_6 (\square). The maximum s -wave electron capture is represented by $\pi\lambda^2$.

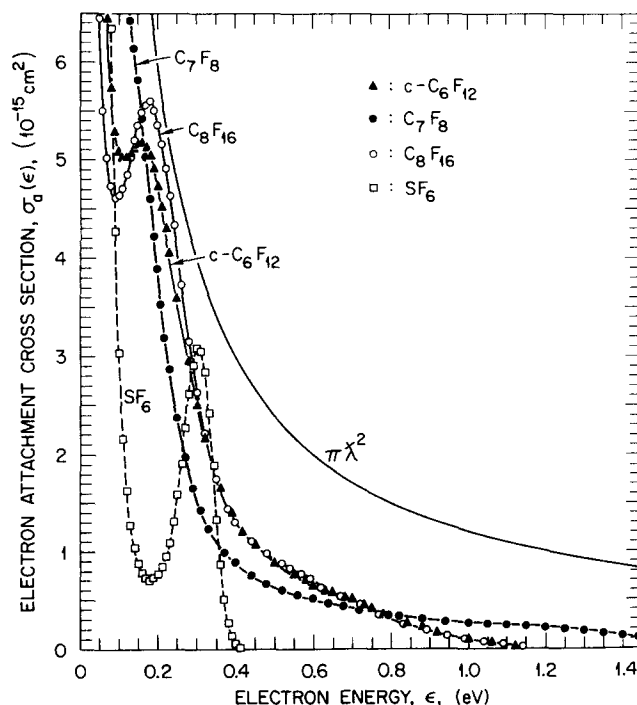


FIG. 4. Electron attachment cross section $\sigma_a(\epsilon)$ as a function of electron energy ϵ for $c\text{-C}_6\text{F}_{12}$ (\blacktriangle), C_7F_8 (\bullet), C_8F_{16} (\circ) and SF_6 (\square). The maximum s -wave electron capture is represented by $\pi\lambda^2$.

TABLE IV. $\sigma_a(\epsilon)$ for $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} .

| Electron energy ϵ (eV) | Electron attachment cross section $\sigma_a(\epsilon)$ (10^{-15} cm^2) | | | | |
|------------------------------------|---|-----------------------------|-----------------------------|------------------------|---------------------------|
| | $c\text{-C}_5\text{F}_8$ | $c\text{-C}_6\text{F}_{10}$ | $c\text{-C}_6\text{F}_{12}$ | C_7F_8 | C_8F_{16} |
| 0.04 | 39.82 | 40.34 | 13.43 | 22.43 | 7.20 |
| 0.06 | 16.51 | 17.66 | 7.94 | 12.58 | 5.53 |
| 0.08 | 6.43 | 8.18 | 5.74 | 8.80 | 4.74 |
| 0.10 | 3.60 | 4.80 | 5.09 | 7.38 | 4.64 |
| 0.12 | 2.64 | 3.58 | 5.03 | 6.74 | 4.86 |
| 0.14 | 2.38 | 3.17 | 5.13 | 6.15 | 5.20 |
| 0.16 | 2.49 | 3.20 | 5.16 | 5.45 | 5.48 |
| 0.18 | 2.73 | 3.34 | 5.04 | 4.61 | 5.60 |
| 0.20 | 3.04 | 3.60 | 4.73 | 3.89 | 5.36 |
| 0.22 | 3.25 | 3.69 | 4.30 | 3.20 | 4.92 |
| 0.24 | 3.35 | 3.61 | 3.82 | 2.62 | 4.34 |
| 0.26 | 3.27 | 3.35 | 3.36 | 2.17 | 3.73 |
| 0.28 | 2.97 | 2.93 | 2.91 | 1.81 | 3.15 |
| 0.30 | 2.56 | 2.44 | 2.51 | 1.54 | 2.64 |
| 0.34 | 1.64 | 1.53 | 1.89 | 1.17 | 1.89 |
| 0.38 | 0.96 | 0.92 | 1.48 | 0.94 | 1.45 |
| 0.42 | 0.59 | 0.61 | 1.21 | 0.81 | 1.20 |
| 0.46 | 0.39 | 0.43 | 1.03 | 0.71 | 1.04 |
| 0.50 | 0.28 | 0.34 | 0.89 | 0.64 | 0.92 |
| 0.55 | 0.22 | 0.30 | 0.77 | 0.57 | 0.81 |
| 0.60 | 0.23 | 0.32 | 0.65 | 0.52 | 0.66 |
| 0.65 | 0.22 | 0.31 | 0.57 | 0.46 | 0.58 |
| 0.70 | 0.24 | 0.32 | 0.50 | 0.42 | 0.49 |
| 0.75 | 0.26 | 0.30 | 0.41 | 0.38 | 0.40 |
| 0.80 | 0.30 | 0.26 | 0.32 | 0.34 | 0.31 |
| 0.85 | 0.34 | 0.19 | 0.25 | 0.31 | 0.23 |
| 0.90 | 0.38 | 0.13 | 0.19 | 0.29 | 0.18 |
| 0.95 | 0.42 | 0.08 | 0.15 | 0.28 | 0.13 |
| 1.00 | 0.43 | 0.04 | 0.10 | 0.26 | 0.10 |
| 1.05 | 0.40 | 0.013 | 0.06 | 0.25 | 0.06 |
| 1.10 | 0.32 | 0.003 | 0.033 | 0.24 | 0.04 |
| 1.15 | 0.22 | | 0.014 | 0.23 | 0.02 |
| 1.20 | 0.12 | | 0.005 | 0.21 | 0.007 |
| 1.25 | 0.05 | | 0.001 | 0.20 | 0.002 |
| 1.30 | 0.017 | | | 0.18 | |
| 1.35 | 0.004 | | | 0.16 | |
| 1.40 | 0.001 | | | 0.13 | |
| 1.45 | | | | 0.11 | |
| 1.50 | | | | 0.08 | |
| 1.55 | | | | 0.06 | |
| 1.60 | | | | 0.04 | |

Except for perfluorotoluene, the $\sigma_a(\epsilon)$ functions have maxima at $\sim 0.15\text{--}0.3$ eV in addition to those at thermal energies and $\sim 0.7\text{--}1.1$ eV. The attachment cross sections for all five compounds studied are $\geq 6 \times 10^{-15} \text{ cm}^2$ at $\epsilon < 0.05$ eV and remain large ($\geq 1 \times 10^{-16} \text{ cm}^2$) in the energy range to ~ 0.8 eV.

C. Thermal ($T \sim 298^\circ\text{K}$) values of the electron attachment rates

Thermal values $(\alpha w)_{\text{ther}}$ of the electron attachment rates as calculated (see Part I) by a convolution of a Maxwellian ($T = 298^\circ\text{K}$) electron energy distribution function with the calculated $\sigma_a(\epsilon)$ functions are listed in Table VI. Also listed in Table VI are the thermal attachment rates determined by a linear extrapolation to $\langle \epsilon \rangle = 0.038$ eV—along with some measured values by Davis *et al.*⁹ The values of $(\alpha w)_{\text{ther}}$ for $c\text{-C}_5\text{F}_8$ and $c\text{-C}_6\text{F}_{10}$ are the largest ever reported. The data of Davis *et al.*⁹ on $c\text{-C}_6\text{F}_{10}$ and C_7F_8 are relatively close to our

results, but their $(\alpha w)_{\text{ther}}$ value for $c\text{-C}_5\text{F}_8$ is a factor of 3 lower. We have no explanation for this large difference.

IV. DISCUSSION

A. Effect of molecular structure on the positions of the negative ion resonances and their respective cross sections

In the preceding paper (Part I), we discussed the effect of molecular structure on the electron attachment properties of perfluorinated four-carbon compounds. The salient features of that discussion are as follows:

(i) Open-chain saturated perfluorocarbons do not attach electrons as efficiently as unsaturated ones.

(ii) For saturated perfluorocarbons, an increase in molecular size (chain length) increases the electron attachment rate.

(iii) The presence of multiple bonds in the molecule dramatically increases the magnitude of the electron attachment rate for saturated open-chain molecules, but it has only a small effect for cyclic perfluorocarbons.

(iv) The cyclic nature of the perfluorocarbons seems to increase greatly their electron capture cross sections.

In this section, we expand on the effects of the perfluorocarbon structure on their electron attaching properties by considering the data on all ten perfluorocarbons studied in Parts I and II.

For all ten aliphatic perfluorocarbons studied in this and the preceding paper, three negative ion resonances have been detected at $\epsilon \leq 1.5$ eV. The structural features of these perfluorocarbons have been systematically varied to determine their effect on the positions and the respective cross sections of the NIR states. Thus, we have altered the cyclobutane ($c\text{-C}_4\text{F}_8$) structure to include a pair of CF_3 groups to give $c\text{-C}_6\text{F}_{12}$ and then we expanded it to a cyclohexane structure (C_6F_{16}). The similarity of $\sigma_a(\epsilon)$ for $c\text{-C}_6\text{F}_{12}$ and C_6F_{16} shows that the size of singly bonded cyclic compounds does not have a strong influence on the energy position of the NIR's or on the magnitude of their respective $\sigma_a(\epsilon)$. In going from $c\text{-C}_4\text{F}_8$ to the more complex compounds, two aspects have been introduced: (i) increased complexity and (ii) addition of CF_3 groups. If, as the $c\text{-C}_6\text{F}_{12}$, C_6F_{16} comparison indicates, increased complexity is not a major factor, then we can attribute the significant increase in the magnitude of $\sigma_a(\epsilon)$ for $c\text{-C}_6\text{F}_{12}$ and C_6F_{16} over that of $c\text{-C}_4\text{F}_8$ at thermal energies to the presence of the CF_3 groups in these structures.

Additionally, we have taken a double-bonded cyclic compound and enlarged it progressively as in the series $c\text{-C}_4\text{F}_6$, $c\text{-C}_5\text{F}_8$, and $c\text{-C}_6\text{F}_{10}$. In this group of perfluorocarbons, increasing the complexity increases the magnitude of the "zero-energy" cross section and the cross section at ~ 0.2 eV. The magnitude of $\sigma_a(\epsilon)$ at higher energies is also increased for $c\text{-C}_5\text{F}_8$ and $c\text{-C}_6\text{F}_{10}$ relative to $c\text{-C}_4\text{F}_6$, but the $c\text{-C}_5\text{F}_8$ cross section is larger at higher energies than the $c\text{-C}_6\text{F}_{10}$ cross section. It may be concluded that in this series of compounds the attachment cross section increases with increasing molecular size.

TABLE V. Electron attachment cross section maxima, values of $\sigma_a(\epsilon)$ at these maxima, energy integrated cross sections, autodetachment lifetimes of the parent negative ions at ~ 0.0 eV, and electron affinities for $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} .

| Molecular formula | ϵ_2^a (eV) | $\sigma_a(\epsilon_2)$ (10^{-15} cm^2) | ϵ_3^a (eV) | $\sigma_a(\epsilon_3)$ (10^{-15} cm^2) | $\int_{0.04 \text{ eV}}^{1.40 \text{ eV}} \sigma_a(\epsilon) d\epsilon$ (10^{-15} eV cm^2) | $RJ_{0.04 \text{ eV}}^{1.40 \text{ eV}}{}^b$ (%) | Lifetime of C_xF_y^- (μsec) | Electron affinity of C_xF_y (eV) |
|-----------------------------|------------------------|---|------------------------|---|---|---|---|---|
| SF_6 | 0.31 | 3.06 | | | 1.17 | 27.5 | 25 ^c 25–35 ^e 68 ^f | $\geq 0.6 \pm 0.1^d$ |
| $c\text{-C}_5\text{F}_8$ | 0.24 | 3.35 | 0.99 | 0.43 | 1.83 | 43.0 | 26.2 ^g 50.0 ^h | |
| $c\text{-C}_6\text{F}_{10}$ | 0.22 | 3.69 | 0.71 | 0.33 | 1.93 | 45.4 | 106 ^g 113 ^h | $\geq 1.4 \pm 0.3^d$ |
| $c\text{-C}_6\text{F}_{12}$ | 0.16 | 5.16 | | | 1.83 | 43.0 | 236 ^g 450 ^h | |
| C_7F_8 | | | ~ 1.1 | 0.24 | 2.01 | 47.2 | 12.2 ^h 37.8 ^g | $\geq 1.7 \pm 0.3^d$ |
| C_8F_{16} | 0.18 | 5.60 | | | 1.76 | 41.5 | | |

^a ϵ_2 and ϵ_3 give the energy position of the second and third maximum, respectively, in $\sigma_a(\epsilon)$; the first maximum is taken at ~ 0.0 eV.

^bSee Sec. III, F of Part I.

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Further, we manipulated the multiple bonding (as in the series $2\text{-C}_4\text{F}_8$, $2\text{-C}_4\text{F}_6$, and $1,3\text{-C}_4\text{F}_6$) to investigate its influence on the magnitude and structure of the attachment cross section functions. Here, increase in multiple bonding rather than increase in size seems to increase $\sigma_a(\epsilon)$ both at thermal energies and at the ~ 0.2

eV peak. The cross sections for the triple bonded $2\text{-C}_4\text{F}_6$ and the twice double bonded $1,3\text{-C}_4\text{F}_6$ extend to slightly higher energies than the singly double-bonded $2\text{-C}_4\text{F}_8$. The position of the third NIR shifts to higher energies (see column 4 of Table V of Part I) with increasing multiple bonding.

TABLE VI. Thermal ($T = 298^\circ\text{K}$) rates for electron attachment to $c\text{-C}_5\text{F}_8$, $c\text{-C}_6\text{F}_{10}$, $c\text{-C}_6\text{F}_{12}$, C_7F_8 , and C_8F_{16} .

| Molecular formula | $(\alpha w)_{\text{meas.}}^a$ at $\langle \epsilon \rangle = 0.046 \text{ eV}$ ($10^9 \text{ sec}^{-1} \text{ torr}^{-1}$) | $(\alpha w)_{\text{ther., unf.}}^b$ at $\langle \epsilon \rangle = 0.038 \text{ eV}$ ($10^9 \text{ sec}^{-1} \text{ torr}^{-1}$) | $(\alpha w)_{\text{ther., extr.}}^c$ at $\langle \epsilon \rangle = 0.038 \text{ eV}$ ($10^9 \text{ sec}^{-1} \text{ torr}^{-1}$) | $(\alpha w)_{\text{ther., lit.}}^d$ ($10^9 \text{ sec}^{-1} \text{ torr}^{-1}$) |
|-----------------------------|--|--|---|--|
| $c\text{-C}_5\text{F}_8$ | 11.62 | 12.80 | 12.60 | 3.82 |
| $c\text{-C}_6\text{F}_{10}$ | 11.88 | 12.92 | 12.85 | 10.14 |
| $c\text{-C}_6\text{F}_{12}$ | 4.73 | 4.98 | 4.93 | |
| C_7F_8 | 8.42 | 9.19 | 9.10 | 7.84 |
| C_8F_{16} | 2.49 | 2.40 | 2.40 | |

^aPresent work. Measured αw values in N_2 for $E/P = 0.02 \text{ V cm}^{-1} \text{ torr}^{-1}$ ($\langle \epsilon \rangle = 0.046 \text{ eV}$) at $T = 298^\circ\text{K}$.

^bPresent work. Calculated thermal values from present $\alpha w(\epsilon)$ data (see Sec. III, E, Part I).

^cPresent work. Determined from two-point extrapolation of the $\alpha w(\epsilon)$ functions to $\langle \epsilon \rangle = 0.038 \text{ eV}$.

^dF. J. Davis, R. N. Compton, and D. R. Nelson, J. Chem. Phys. **59**, 2324 (1973).

TABLE VII. Direct current relative dielectric strengths for perfluorocarbons.

| Compound | | dc Relative dielectric strength ^{a,b} |
|-----------------------------------|-------------------------------------|--|
| SF ₆ | | 1.0 |
| c-C ₄ F ₈ | (perfluorocyclobutane) | 1.3–1.4 |
| 2-C ₄ F ₈ | (perfluoro-2-butene) | 1.7–1.8 |
| 1,3-C ₄ F ₆ | (perfluoro-1,3-butadiene) | 1.4 |
| c-C ₄ F ₆ | (perfluorocyclobutene) | 1.7 |
| 2-C ₄ F ₆ | (perfluoro-2-butyne) | 2.2 |
| c-C ₅ F ₈ | (perfluorocyclopentene) | 2.1–2.2 |
| c-C ₆ F ₁₀ | (perfluorocyclohexene) | 1.9–2.2 |
| c-C ₆ F ₁₂ | (perfluoro-1,2-dimethylcyclobutane) | 2.3–2.4 |
| C ₇ F ₈ | (perfluorotoluene) | ~2.4 |
| C ₈ F ₁₆ | (perfluoro-1,3-dimethylcyclohexane) | ~2.4 |

^aSphere-plane electrode geometry.^bFrom Refs. 2 and 4.

B. Relevance to gaseous dielectrics— the significance of negative ion resonances and electron attachment and the concept of multicomponent gaseous insulators

Over the past two decades, investigations of the interactions of slow electrons with molecules have led to the recognition of the importance of negative ion resonances in low-energy electron-molecule collisions. Not only are the numbers and the positions of such resonances strong functions of the molecular structure, but the magnitude of their respective cross sections can be very large compared to other “direct” scattering processes which can occur in electron-molecule collisions.

The NIR's can be efficient mechanisms for molecular rotational and vibrational excitation. They decay by electron emission and also, if energetically possible, by dissociative attachment; if the electron affinity of the molecule is positive and the excess energy removed, they can lead to stable parent negative ions. The NIR's are often described in terms of the molecular orbital(s) which the attached electron occupies.¹⁰

The NIR's play two important roles in improving the dielectric strength of gases which possess them.³ For those gases—such as N₂, H₂, etc.—which do not have positive electron affinities, NIR's are efficient mechanisms for removing energy from the electrons and thus inhibiting breakdown by an overall shift to lower energies of the electron energy distribution function in the gas under electrical stress.³ (The direct effect of these resonances on the dielectric strength of gases has been demonstrated.^{1–6}) For those compounds with positive electron affinities, such as the perfluorocarbons studied in this and the preceding paper, NIR's allow the efficient capture of electrons, especially at energies from 0.0 to ~1.5 eV. The extension of the electron attachment cross section to higher energies allows a larger overlap of the attachment cross section with the electron energy distribution function and consequently more efficient electron attachment at higher electrical stresses (see discussion in Refs. 1–6).

All of the perfluorinated hydrocarbons studied in this

and the preceding paper have been tested as gaseous dielectrics.^{1–6} In a direct comparison with sulfur hexafluoride (SF₆) under identical conditions (same electrode geometry, electrode separation, gas pressure, and temperature), they withstood between 1.4 and 2.4 times the dc voltage before breakdown as did SF₆ (see Table VII). These perfluorocarbon gases divide into two groups. In one group, the dielectric strength V_s is between 1.3 and 1.8 times that of SF₆. In the other group, V_s is between 2.1 and 2.4 times that of SF₆. The first group is comprised only of four-carbon containing compounds. These all have vapor pressures greater than 1 atm at room temperature and are good candidates as dielectric gases. In the second group, the molecules (with the exception of 2-C₄F₆) are more complex.

Although such increased complexity decreases vapor pressures—and practical applications require higher vapor pressures than those these compounds possess—they can be used in dielectric mixtures in combination with other gases.^{1–6} There seems to be no straightforward correlation between the structure of these compounds and their dielectric strength although the energy integrated attachment cross sections for the higher dielectric strength group are generally higher and both the attachment cross sections and dielectric strengths increase with increasing molecular complexity. (See Ref. 3 for a discussion of the effects of the microscopic molecular characteristics on V_s and Ref. 11 as to the significance of perfluorination.) The higher breakdown strength of 2-C₄F₆ compared to the other four-carbon containing compounds has been attributed^{1–6} to the extension of its $\sigma_a(\epsilon)$ to higher energies (see Fig. 8 of Part I) and to the presence of the triple bond which should affect (lower) the mean electron energy and shift the electron distribution to lower energies (see Refs. 2–4 and discussion later in this section).

The high dielectric strength of all ten perfluorocarbons studied in this paper and in Part I is large by virtue of their high $\sigma_a(\epsilon)$.^{1–5,11} As it has been discussed earlier^{1–5,11} and is elaborated upon below, indirect inelastic electron scattering via NIR's and large electron attachment cross sections over a wide energy range

above thermal energy crucially affect the breakdown strength of the dielectric.

In a gas discharge, the single most important parameter which determines the onset voltage of the discharge is the number density n_e of the free electrons in the gas. The rate of change of this quantity in a gas under an applied electric field is governed by the difference between the total ionization and the total electron attachment. These two quantities are related to the ionization cross section $\sigma_i(\epsilon)$, attachment cross section $\sigma_a(\epsilon)$, and the electron energy distribution function $f(\epsilon)$ by

$$\text{total ionization} \propto \int_I^\infty \sigma_i(\epsilon) f(\epsilon) d\epsilon, \quad (1)$$

$$\text{total attachment} \propto \int_0^\infty \sigma_a(\epsilon) f(\epsilon) d\epsilon, \quad (2)$$

where I is the ionization threshold energy. Given $\sigma_i(\epsilon)$ and $\sigma_a(\epsilon)$, $f(\epsilon)$ determines the values of net ionization (1) and net attachment (2). The distribution function is determined by the cross sections for elastic and inelastic electron scattering (especially through NIR states²⁻⁵) and to some extent by the attachment and ionization cross sections. Recently, we^{5,11} have obtained experimental evidence that the dielectric strength of a gas is more crucially affected by $\sigma_a(\epsilon)$ and the electron scattering cross sections determining $f(\epsilon)$, rather than by the ionization cross sections $\sigma_i(\epsilon)$.

Besides the present measurements on $\sigma_a(\epsilon)$ and some electron impact ionization cross section studies (see Refs. 5 and 11), no other cross section data exists on the interactions of slow electrons with the perfluorocarbons under consideration. For two of the perfluorocarbons studied—2-C₄F₈ and *c*-C₄F₈—the related “gross” quantities $\langle \alpha \rangle$ (mean ionization coefficient), $\langle \eta \rangle$ (mean attachment coefficient), w (electron drift velocity), and D_L/μ (ratio of lateral electron diffusion coefficient to electron mobility) have been measured by Naidu *et al.*¹² as a function of E/P in the range 90–210 and 140–270 V cm⁻¹ Torr⁻¹ for *c*-C₄F₈ and 2-C₄F₈, respectively.¹³ In these E/P ranges, the D_L/μ values for 2-C₄F₈ are lower than for *c*-C₄F₈. The smaller D_L/μ values are then reflected in the higher η 's and the lower α 's for 2-C₄F₈ over this E/P range through the fact that in Eqs. (1) and (2) a lower D_L/μ (i. e., a lower mean electron energy) implies a lower electron energy distribution $f(\epsilon)$ which would reduce Eq. (1) and increase Eq. (2) since $\sigma_i(\epsilon)$ is nonzero only above I and $\sigma_a(\epsilon)$ is highest at low energies.³ The $D_L/\mu(E/P)$ data of Naidu *et al.*¹² and the present $\sigma_a(\epsilon)$ measurements for *c*-C₄F₈ and 2-C₄F₈ could explain the superior V_s of 2-C₄F₈ over *c*-C₄F₈. Similar arguments could be advanced for the superior behavior of 2-C₄F₈ compared to the rest of the four-carbon containing perfluorocarbons in Table VII.

The previous^{1-6,11} and the present work underlines on the one hand the importance of effective electron scattering at low (subexcitation) energies to shift the electron energy distribution function to lower energies so that ionization is decreased and electron attachment is increased and, on the other hand, the importance of

large $\sigma_a(\epsilon)$ to high ϵ to allow maximum reduction in the electron density by optimizing the overlap of $\sigma_a(\epsilon)$ and $f(\epsilon)$.

Since a given molecule may not possess both large electron scattering and electron attachment cross sections over a wide energy range, it is unlikely that there is an optimum single gas as a dielectric. We have argued^{1-6,11} that it is in gas mixtures and on the basis of detailed knowledge on the magnitude and energy dependence of the slow electron-molecule collision processes that one would look to optimize both Eqs. (1) and (2). By introducing one or more component gases to shift $f(\epsilon)$ to low energies, where $\sigma_a(\epsilon)$ are the largest and one or more component gases to effect a $\sigma_a(\epsilon)$ as high as possible over as wide an energy range as possible, the dielectric capabilities of a gas mixture can be optimized.¹⁻⁶ A number of such mixtures with potential for practical application¹⁻⁶ and with superior properties to SF₆ have been developed in this manner (see Refs. 1–6 and 11).

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