# Measurement of the electron attachment rates for $SF_6$ and $C_7F_{14}$ at $T_e$ =0.2 eV in a magnetized Q machine plasma

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Electron attachment rates for SF<sub>6</sub> and  $C_7F_{14}$  were measured in a magnetized Q machine plasma at an electron temperature of  $0.2\pm0.02\,$  eV and with neutral gas pressures of  $P\sim10^{-4}\,$  Torr. The rate constants for attachment to SF<sub>6</sub> and  $C_7F_{14}$  were  $(7.6\pm2.0)\times10^{-8}\,$  and  $(2.2\pm0.9)\times10^{-7}\,$  cm<sup>3</sup> s<sup>-1</sup>, respectively. © 2008 American Institute of Physics. [DOI: 10.1063/1.3039078]

#### I. INTRODUCTION

Experimental studies on electron attachment to sulfur hexafluoride (SF<sub>6</sub>) and perfluoromethylcyclohexane (C<sub>7</sub>F<sub>14</sub>) have been performed by a number of groups using a variety of techniques. The continuing interest in perfluorocarbons is due to their practical value as gaseous insulators and the need to understand the role of electron attachment in increasing their dielectric strength. Early studies on electron attachment to SF<sub>6</sub> and C<sub>7</sub>F<sub>14</sub> include the electron beam studies of Asundi and Craggs,<sup>2</sup> who obtained the cross sections for both electron capture and ionization, and measurements of the attachment rate constants at  $T_e$ =300 K using a microwave cavity technique by Mahan and Young,<sup>3</sup> and pulsesampling techniques by Chen et al. 4 An important issue, both from the point of view of the basic chemical physics of electron/molecule interactions, as well as technical applications, is how the attachment rates depend on electron temperature or mean electron energy. This is of particular importance in understanding the role of electron attachment in the lower ionosphere where the electron temperature is in the range of 1000-2000 K.

#### A. SF<sub>6</sub>

Smith et al., using the flowing afterglow/Langmuir probe (FALP) method, reported that there was an indication of a peak in the attachment rate  $k_a$  within the 400-500 K range. Subsequent measurements of Petrović and Crompton,<sup>6</sup> using the Cavalleri electron density sampling technique, which is considered to be one of the most accurate methods for the determination of attachment rate constants, did not support the temperature dependence seen by Smith et al.<sup>5</sup> and showed that the attachment rates at 300 and 500 K were the same within the error bounds. Klar et al., using the laser photoelectron method, measured electron attachment to SF<sub>6</sub> in the energy range of 0-200 meV with sub-meV resolution and found energy-dependent rate constants that decreased with electron energy in this range. Datskos et al., using a time-resolved electron swarm technique, also reported electron attachment rate constants for SF<sub>6</sub> that decreased with mean electron energy in the range of 0.2-1.0 eV. Braun et al. obtained electron attachment rates for electron energies up to 200 meV using the laser photoelectron attachment method for various nozzle temperatures of the helium carrier gas. The attachment cross section for SF<sub>6</sub> decreased by five orders of magnitude over the energy range of 1-500 meV, with little effect of changing the nozzle temperature in the range of 300-600 K. Recent FALP measurements by Viggiano et al., <sup>10</sup> of attachment rate coefficients for SF<sub>6</sub>, were in excellent agreement with the results of Petrović and Crompton. Electron attachment rates for SF<sub>6</sub> in the range of 200-600 K obtained from calculated cross sections showed good agreement with the experimental measurements in Ref. 6 and poorer agreement with those in Ref. 5. An extended study on the electron temperature dependence of the attachment rate was performed by Spanel et al. 11 using the FALP technique with argon rather than helium as the buffer gas allowing electron temperatures up to about 4000 K to be achieved. The FALP attachment rate at 300 K, reported by Spanel et al., 11 was smaller than the original FALP value of Smith et al.<sup>5</sup> but only slightly (13%) above the value of Petrović and Crompton.

### B. C<sub>7</sub>F<sub>14</sub>

Mahan and Young<sup>3</sup> determined the attachment rate at 300 K but noted that the rate constant remained unchanged or slightly increased if the electron temperature was increased. This conclusion was supported by measurements of Chen et al.4 using the pulse sampling technique. Davis et al., 12 using an electron swarm method, reported a thermal attachment rate which increased with increasing mean energy of the electron swarm. Using a similar swarm technique, Christodoulides and Christophorou<sup>13</sup> studied electron attachment in both l- and c-C<sub>7</sub>F<sub>14</sub> up to electron energies of about 3 eV. For both molecules, the attachment cross sections showed resonance maxima at 0.07 and 0.25 eV, and they were much larger for the cyclic isomer. Alge et al. 14 studied electron attachment using the FALP method in the electron temperature range of 200-600 K under truly thermalized conditions in which both the carrier gas and attaching gas were at the same temperature. They found that the attachment rate increased with increasing  $T_e$  and approached theoretical maximum value <sup>15,16</sup> of  $\times 10^{-7} (300/T_e)^{1/2}$  cm<sup>3</sup>/s at the higher temperatures.

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Chutjian and Alajajian<sup>17</sup> performed attachment measurements using the threshold photoionization method over the energy range of 0-160 meV. Attachment rates  $k_a(\bar{\epsilon})$  as a function of mean electron energy  $\bar{\varepsilon}$  were derived from the measured cross sections and compared with the results of Davis et al., <sup>12</sup> Christodoulides and Christophorou, <sup>13</sup> and Alge et al. 14 Chutjian and Alajajian 17 found a broad peak in  $k_a(\bar{\epsilon})$  at around 100 meV, which was in general agreement with the results of Davis et al. 12 but in disagreement with those of Christodoulides and Christophorou<sup>13</sup> and Alge et al. 14 Walter et al. 18 obtained attachment cross sections for C<sub>7</sub>F<sub>14</sub> in the 1–100 meV range through studies of high Rydberg K(nd)-C<sub>7</sub>F<sub>14</sub> collisions. The cross section at 1 meV was  $\sim 2 \times 10^{-14} \text{ cm}^2$  and decreased monotonically thereafter. These results were in agreement with those in Ref. 17 but differed substantially with those in Ref. 13, which showed a peak in the cross section at 70 meV. Shimamori et al. 19 measured attachment rate constants for C<sub>7</sub>F<sub>14</sub> from thermal energies to about 1 eV using a microwave cavity/pulse radiolysis method. The rate constant peaked at mean electron energy of 0.2 eV. The energy dependence of  $k_a$  was similar to that found by Christodoulides and Christophorou<sup>13</sup> but with a peak value that was about 30% lower. Spanel et al. 11 reported new FALP measurements of electron attachment constants over an extended electron temperature range from 300 to about 4000 K.4 In contrast to the earlier FALP measurements of Alge et al., 14 which were conducted under truly thermalized conditions  $(T_e = T_{gas})$ , the present experiment was carried out with  $T_{\rm gas}$ =300 K. The rate constants were substantially lower than those of Alge et al. 14 in the temperature range common to both sets of measurements. The results of Spanel et al. 11 are interesting because they showed that in systems in which activation barriers exist to the attachment process, the required activation energy can be supplied either by going to higher electron temperatures or by increasing the vibrational temperature of the molecule.

Here we report a direct comparison of measurements of the electron attachment rates of SF<sub>6</sub> and C<sub>7</sub>F<sub>14</sub> in a plasma at an electron temperature of  $T_e \approx 0.2$  eV. The experimental apparatus (Q machine<sup>20</sup>) used is somewhat similar to the FALP apparatus <sup>15,16</sup> in that it uses a localized plasma source at one end of a long cylindrical vacuum chamber and a Langmuir probe (LP) to measure the reduction in electron density along the axis of the device when an electron-attaching species is present. The Q machine differs from the FALP device in that the plasma is magnetized, no carrier or buffer gases are used, and the pressures of the attaching gases are ≤10<sup>-4</sup> Torr. At the low pressures and high magnetic strengths used, the effects of radial diffusion of the electrons in the Q machine are relatively unimportant. This is in contrast to the FALP technique in which the effects of diffusion are often significant and a detailed analysis is required to obtain electron attachment rates from the electron density gradient.

#### II. EXPERIMENTAL

A schematic of the experimental setup, which has been discussed in detail previously, 21 is shown in Fig. 1. The

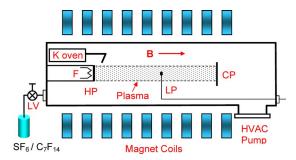


FIG. 1. (Color online) Schematic of the experimental device. The plasma is produced by surface ionization of potassium atoms on a hot tantalum plate. The plasma is confined radially by a magnetic field up to 0.5 T and is terminated on a floating cold plate. The electron density and temperature are measured with a planar LP, which is movable in the radial direction and along the plasma column. Electron attachment rates are inferred from measurements of the spatial gradient of the electron density when the electron attaching gases are introduced.

plasma device is a Q machine<sup>20</sup> in which potassium atoms from an atomic beam oven are formed by contact ionization (the capture of a valence electron from an atom by a metal surface<sup>22</sup>) on the surface of a 6 cm diameter electrically grounded tantalum hot plate (HP). The HP is heated to ~2200-2400 K by bombardment of electrons emitted by a spiral filament located behind the plate. The HP also emits thermionic electrons and together with the K<sup>+</sup> ions form a nearly fully ionized plasma that is  $\sim 1$  m in length and 6 cm in diameter. The plasma is confined radially by a uniform magnetic field with a maximum strength of 0.5 T, which is provided by a set of water-cooled solenoid coils powered by a direct current supply. The plasma is terminated on an electrically floating cold end plate. The stainless steel vacuum vessel, approximately 2 m in length and 33 cm in diameter, is cooled to -10 °C to maintain the neutral K pressure <10<sup>-6</sup> Torr. The electron density and temperature were measured with a planar (disk) LP that could be moved radially and axially. The plasma ion density  $(n_{+})$ , determined from the ion saturation current to the LP, was  $\sim 10^9$  cm<sup>-3</sup>. Due to the strong magnetic field and relatively infrequent collisions, electron diffusion out of the plasma column is strongly inhibited.<sup>23</sup>

A typical example of a LP current (I) versus voltage (V)characteristic used for the determination of the electron temperature is shown in Fig. 2(a). The positive current in this plot is the electron current collected by the probe. The electron temperature was obtained from the probe characteristic by the following method. The space or plasma potential is first determined as the voltage at which  $d^2I/dV^2$  equals zero. A linear fit is made to the positive ion current, which is then subtracted from the total current to obtain the electron current. A semilog plot of the electron current in the retarding potential region (below the plasma potential) is shown in Fig. 2(b). A plot of log I versus V will be linear in the retarding potential region for a Maxwellian plasma, and the electron temperature is determined from the slope of this line. The solid line in Fig. 2(b) is the exponential fit from which we obtained  $k_B T_e \approx 0.20 \pm 0.02$  eV.

The electron attaching species,  $SF_6$  or  $C_7F_{14}$ , were leaked into the system through a fine needle valve (LV in

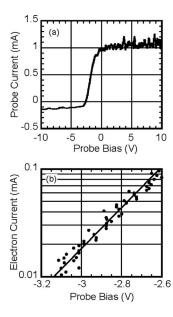


FIG. 2. LP measurements of the electron temperature. (a) Probe current-voltage characteristic I(V). The positive current is the electron current in this plot. (b) Semilogarithmic plot of the electron current in the retarding potential region. The solid line is the exponential fit to the data from which the electron temperature  $T_e$  is inferred.

Fig. 1). The C<sub>7</sub>F<sub>14</sub> liquid was degassed using several pressure reduction cycles. The SF<sub>6</sub> and C<sub>7</sub>F<sub>14</sub> reservoirs were maintained at room temperature and we assume that they remain close to room temperature when they are added to the plasma. At the pressures used in this experiment, the mean free paths of the molecules within the system are on the order of the length of the chamber, so there is not enough time for the molecules to heat up or cool down due to conduction with the chilled walls or the HP. We estimated also that heat transfer to the molecules by radiation from the HP would not significantly raise the gas temperature. The pressures of the attaching gases were measured with a Bayard-Alpert ionization gauge. The gas sensitivity factors for SF<sub>6</sub> and C<sub>7</sub>F<sub>14</sub> were determined by calibrating the ionization gauge against an absolute pressure capacitance manometer.<sup>24</sup> The measured gas sensitivity factor for  $SF_6$  (2.3) was in good agreement with the average value provided by the gauge manufacturer. No gas sensitivity factor for C<sub>7</sub>F<sub>14</sub> was available so we used the value of 6.4, which was obtained from the capacitance manometer calibration. We estimate the uncertainty in the absolute pressure measurements to be 15%. Based on our estimates of the maximum possible change in the gas temperature within the vacuum vessel, we place the overall uncertainty in the determination of the gas density to be 25%.

## **III. RESULTS AND DISCUSSION**

#### A. Electron attachment measurements

Electron attachment rates were determined from LP measurements of the axial gradient of the electron density when the attaching gas was introduced. The attaching gases were continuously leaked into the vacuum system at steady pressures and the variation in the electron density along the axis of the plasma column  $n_e(z)$  was measured with the LP. The

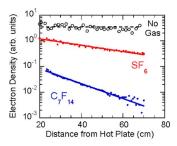


FIG. 3. (Color online) Decay of the electron density  $n_e$  along the axis of the plasma when SF<sub>6</sub> or  $C_7F_{14}$  is introduced. The uppermost plot (open circles) is the electron density in the absence of any attaching gas. B=0.3 T. The HP is located at z=0.

data were fitted to an exponential  $n_e(z) = n_e(0) \exp(-\alpha z)$  to obtain the spatial decay rate  $\alpha$ . The electron attachment rate  $k_a$  was determined from the spatial decay rates using  $k_a = \alpha v_{eT}/N_a$ , where  $v_{eT} = (k_B T_e/m_e)^{1/2}$  is the electron thermal speed (with  $k_B T_e = 0.2$  eV) and  $N_a$  is the density of the attaching species.

#### 1. SF<sub>6</sub>

A semilogarithmic plot of the electron density  $n_e(z)$  along the axis of the plasma when SF<sub>6</sub> was introduced at a pressure of  $P=2.2\times10^{-4}$  Torr is shown in Fig. 3. The upper plot (open circles) in Fig. 3 is  $n_e(z)$  when no attaching gases were added to the plasma. The spatial decay rate obtained from the fitting routine was  $\alpha(\text{SF}_6)=0.029$  cm<sup>-1</sup>. The resulting electron attachment rate constant for SF<sub>6</sub> at  $T_e=0.2$  eV was

$$k_a(SF_6) = (7.6 \pm 2.0) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$$

where the uncertainty is the aggregate of the uncertainties in the gas density, electron temperature, and spatial decay rate.

There have been very few measurements of attachment rates for SF<sub>6</sub> at electron temperatures above about twice the room temperature. Spanel et al. 11 measured attachment rates for SF<sub>6</sub> up to about 4000 K using the FALP technique. Their measurements at lower temperatures (300–500 K) were in agreement with the previous best measurements of Petrović and Crompton<sup>6</sup> who reported a  $k_a = (2.27 \pm 0.07)$  $\times 10^{-7}$  cm<sup>3</sup>/s at 300 K as well as recent measurements of Viggiano et al. 10 Both Petrović and Crompton and Viggiano et al. 10 found only a small decrease in  $k_a$  in the temperature range of 300-670 K. Our result for SF<sub>6</sub> at  $T_e \approx 0.2$  eV agrees with those of Spanel *et al.*<sup>11</sup> who found a  $k_a \approx 8$  $\times 10^{-8}$  cm<sup>3</sup>/s at roughly the same temperature. The decrease in  $k_a$  at temperatures above thermal is also consistent with the swarm measurements of Datskos et al.8 who found that at a mean electron energy of 0.2 eV,  $k_a \approx 9 \times 10^{-8}$  cm<sup>3</sup>/s. Our result is also in line with the recommended value with a value of  $0.801 \times 10^{-7}$  cm<sup>3</sup> s<sup>-1</sup> at  $\bar{\epsilon}$ =0.2 eV given by Christophourou and Olthoff.<sup>26</sup>

A plot of the measured attachment rate at  $T_e$ =0.2 eV, along with rates reported by a number of other workers at various values of either the electron temperature or, in some cases, mean electron energy, is shown in Fig. 4. The present value falls in line with the trend of the attachment rates that decrease with increasing electron temperature.

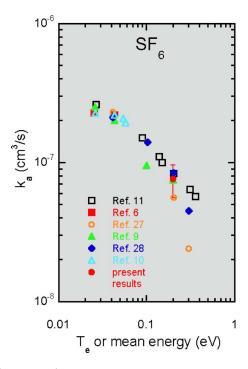


FIG. 4. (Color online) Rate constants for electron attachment to SF<sub>6</sub> as a function of electron temperature or mean electron energy. Present results—solid circle with error bar; solid squares—Ref. 6; solid upward triangles—Ref. 9; open triangles—Ref. 10; open squares—Ref. 11; open circles—Ref. 27; and solid diamonds—Ref. 28.

# 2. C<sub>7</sub>F<sub>14</sub>

The spatial variation in the electron density along the plasma column when  $C_7F_{14}$  was added at a pressure of  $P=1.9\times 10^{-4}$  Torr is shown in Fig. 3. The decay rate obtained from the exponential fitting function was  $\alpha(C_7F_{14})=0.070~{\rm cm}^{-1}$ . The resulting electron attachment rate constant for  $C_7F_{14}$  at  $T_e=0.2~{\rm eV}$  was

$$k_a(C_7F_{14}) = (2.2 \pm 0.9) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1},$$

where, again, the quoted uncertainty represents the aggregate of the uncertainties in the gas density, electron temperature, and spatial decay rate.

The measured rate constant for C<sub>7</sub>F<sub>14</sub> was almost three times as large as the corresponding value for SF<sub>6</sub>. Mahan and Young,<sup>3</sup> using a microwave cavity resonance technique, reported a rate constant of  $9.8 \times 10^{-8}$  cm<sup>3</sup>/s at 300 K with a maximum error estimate of 25%. They noted a slight increase in the rate constant with increasing temperature. Their value was supported by measurements of Chen et al. 4 using a pulse-sampling technique also at 300 K. In an electron swarm experiment Davis et al. 12 found a strong dependence of the rate constant on electron energy above thermal rate constant values. They found a value of  $k_a(C_7F_{14})=7.39$  $\times 10^{-8}$  cm<sup>3</sup>/s at the mean electron energy of 0.16 eV, which was the highest energy measured. They also noted that C<sub>7</sub>F<sub>14</sub> is a special case in which  $k_a$  increases with increasing electron energy above the thermal value. Swarm studies were extended to mean electron energies of 3 eV by Christodoulides and Christophorou, <sup>13</sup> who found a rate constant which peaked at a mean electron energy of about 0.2 eV at  $k_a$  $\approx 1.4 \times 10^{-7}$  cm<sup>3</sup>/s. Shimamori *et al.*<sup>19</sup> carried out a similar

set of experiments on the dependence of the attachment rate constants with mean electron energy using a pulse-radiolysis microwave cavity technique. Their rate constants showed very similar dependence on electron energy as those of Christodoulides and Christophorou, 13 although the peak value of the attachment rate was about half of that of Christodoulides and Christophorou. 13 Chutjian and Alajajian<sup>17</sup> reported electron attachment cross section measurements from ultralow electron energies (with meV resolutions) up to 160 meV. They integrated their cross sections with a Maxwellian distribution function to obtain attachment rates as a function of the mean energy  $\bar{\epsilon}$ . Their attachment rates increased with  $\bar{\epsilon}$  up to a peak value of  $(5\pm1)$  $\times 10^{-8}$  cm<sup>3</sup>/s at  $\bar{\epsilon} \approx 100$  meV. They commented that the difference between their results and the swarm results of Christodoulides and Christophorou<sup>13</sup> might be related to non-Maxwellian or nonequilibrium conditions that could be present in the swarm experiments. The results of Chutjian and Alajajian, <sup>17</sup> however, were supported by the Rydberg atom collision studies of Walter et al. 18 Finally we compare our results to the 1995 FALP results of Spanel et al. 11 who measured attachment rates for a number of selected molecules including SF<sub>6</sub> and C<sub>7</sub>F<sub>14</sub> from 300 to about 4000 K. The rate coefficient for the direct attachment of electrons to C<sub>7</sub>F<sub>14</sub> increased with increasing electron temperature, with a particularly sharp increase from about 0.1 to 0.3 eV. At the electron temperature of  $\sim 0.2\,$  eV, they obtained a rate coefficient of  $k_a \approx (9.5 \pm 1.5) \times 10^{-8}$  cm<sup>3</sup>/s, which is in reasonable agreement with the value obtained in the present experiment. We note that the results of Spanel et al. 11 for SF<sub>6</sub> were about 10% higher than the accurate results of Crompton and co-workers. 6,29

For comparison, our value of  $k_a$  for  $C_7F_{14}$  at 0.2 eV, along with those obtained by other methods as a function of electron temperature or mean electron energy, is shown in Fig. 5. Compared with the data for  $SF_6$ , the  $C_7F_{14}$  results show considerably greater spread. However, there is a general trend of the attachment rate increasing with  $T_e$  from its value at 300 K.

# B. Identification of the negative ions and lifetime estimates

When an electron current is drawn along the magnetic field to a LP in the plasma, an ion-cyclotron instability is excited,  $^{30}$  which produces coherent plasma density oscillations at a frequency slightly above the ion-cyclotron frequency  $f_{c\pm}=eB/2\pi m_{\pm}$ , where  $m_{\pm}$  is the positive/negative ion mass of both the positive and negative ions. The presence of peaks at specific frequencies in the spectrum of oscillations of the electron current was used to identify the formation of both  $SF_6^-$  and  $C_7F_{14}^{-}$ .

In addition to providing a means of identifying the negative ions present in the plasma, the fact that coherent negative ion-cyclotron oscillations were observed implies that the negative ions were stable against autodetachment for at least several ion-cyclotron periods,  $T_{c-}=f_{c-}^{-1}=2\pi m_{-}/eB$ . For SF<sub>6</sub>,  $T_{c-}=32~\mu s$ , while for  $C_7F_{-4}^-$ ,  $T_{c-}=77~\mu s$ . In fact, the ion-cyclotron period is only a lower limit to the negative ion

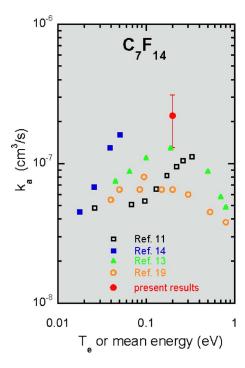


FIG. 5. (Color online) Rate constants for electron attachment to  $C_7F_{14}$  as a function of electron temperature or mean electron energy. Present results—solid circle with error bar; open squares—Ref. 11; closed triangles—Ref. 13; closed squares—Ref. 14; and open circles—Ref. 19.

lifetime because typically, the growth time for the ion-cyclotron instability is  $\sim (10-50)T_{c-}$ , <sup>32</sup> which would require lifetimes of approximately a millisecond.

#### **IV. CONCLUSIONS**

Attachment rates for both  $SF_6$  and  $C_7F_{14}$  at pressures of  $P \sim 10^{-4}$  Torr have been measured at an electron temperature of  $0.2 \pm 0.02$  eV in a magnetized Q machine plasma. The attachment rate at 0.2 eV for  $C_7F_{14}$  was close to the theoretical s-wave limit and more than twice as large as that of  $SF_6$ . The reasonable agreement between the present results and those obtained by other methods demonstrates the potential for using the Q machine for electron attachment measurements, which was one of our goals in performing this experiment.

Miller *et al.*<sup>33</sup> recently pointed out the need for additional studies on electron attachment to  $SF_6$  and detachment from  $SF_6^-$  in the  $\mu$  Torr and mTorr pressure range, as well as at higher temperatures. In future work, we plan to examine the pressure dependence of the attachment rate constants as well as attempt to detect the presence of  $SF_5^-$  formed by dissociative attachment. Finally, we point out that thermal and nonequilibrium distributions may yield quite different results, and with cross sections weighed toward low energies and some dissociative attachment and vibrational losses lim-

iting the nonequilibrium distribution functions at high energies, the attachment rates could be quite different.<sup>34</sup>

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