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Dissociative electron attachment to C$_2$F$_5$ radicals

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Dissociative electron attachment to the reactive C$_2$F$_5$ molecular radical has been investigated with two complimentary experimental methods; a single collision beam experiment and a new flowing afterglow Langmuir probe technique. The beam results show that F$^-$ is formed close to zero electron energy in dissociative electron attachment to C$_2$F$_5$. The afterglow measurements also show that F$^-$ is formed in collisions between electrons and C$_2$F$_5$ molecules with rate constants of $3.7 \times 10^{-9}$ cm$^3$ s$^{-1}$ to $4.7 \times 10^{-9}$ cm$^3$ s$^{-1}$ at temperatures of 300–600 K. The rate constant increases slowly with increasing temperature, but the rise observed is smaller than the experimental uncertainty of 35%.

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I. INTRODUCTION

Low temperature technological fluorocarbon plasmas are used widely in industry, for example, to etch silicon dioxide in semiconductor processing and to deposit hydrophobic polymeric fluorocarbon layers. Such technological plasmas are, of course, chemically potent as they contain free electrons, positively and negatively charged ions, atoms, radicals, and excited states. The dynamics and chemistry of plasmas are complex. It has been stated that the main roadblock in the development of plasma models is a lack of fundamental data for the atomic and molecular processes that occur in plasmas. In particular, data for radicals, reactive molecules and excited states have been highlighted as a particular area of need. These species are critical to the overall chemical and physical processes occurring in the plasma, but on the other hand they are so reactive that for experimental investigations they generally need to be generated in situ and gas samples may be impure.

Collisions between low energy electrons and molecules can lead to the formation of negative ions through associative electron attachment and dissociative electron attachment. Both of these processes commence with the electron, $e^-$, becoming attached to the molecule, say AB, to form a superexcited anionic state of the molecule, AB$^{-\ast}$, thus

$$AB + e^- \rightarrow AB^{-\ast}. \quad (1)$$

The anion, AB$^{-\ast}$, is superexcited because when it is first formed the combined energy of the free electron and the neutral molecule is necessarily higher than the ionization energy of the anion, AB$^-$. Therefore, an electron can readily be lost from AB$^{-\ast}$ in autodetachment, which can also be described as autoionization. If, however, the electron becomes attached in, for example, a shape resonance or Feshbach resonance then it may be trapped on the molecule long enough for the nuclei to move and for the molecule to dissociate by

$$AB^{-\ast} \rightarrow A + B^-, \quad (2)$$

where A and B$^-$ may be atoms or multiatomic molecular fragments. This overall process of electron capture and molecular fragmentation is dissociative electron attachment. In some special cases, most famously SF$_6$, electrons with close to zero kinetic energy can attach to form superexcited states with lifetimes in the microsecond, millisecond or even second range. It is possible to detect negatively charged parent ions, such as SF$_5^-$ in such cases. Such close to zero energy electron attachment processes can have very large cross sections; for example, electron attachment to SF$_6$ has a cross section of over 1000 Å$^2$ at 1 meV collision energy.

Plasmas contain high densities of low energy free electrons and, thus, such low energy attachment processes can play a very important role in the overall behaviour of plasmas.

Laboratory investigations of electron attachment to molecules can be split into two main groups; single collision experiments and multiple collision experiments. In single collision experiments a beam of electrons with well defined energy interacts with the molecular target at low pressure. In multiple collision experiments, electrons and molecules interact together in a buffer gas and electron attachment rate constants are measured at the well defined temperature of the buffer gas, which can be varied. These two methods are complimentary and both have been used in the present investigation of electron attachment to the radical C$_2$F$_5$.

Previous investigations of electron attachment to reactive molecules and radicals include R-matrix calculations of low energy electron collisions with CF$_5$ and CF$_2$ and CF$_3$. Dissociative electron attachment to CF$_2$ was investigated experimentally, but no attachment was observed. Elastic electron scattering from CF$_2$ has been observed and reported with...
Schwinger multichannel variational calculations. Both these R-matrix\(^7\) and Schwinger calculations\(^{11}\) for CF\(_2\) agree with another Schwinger calculation\(^{12}\) in the prediction of a low energy electron attachment resonance at 1.5 eV or lower electron energy. This low energy resonance has not been observed experimentally because elastic scattering measurements have not been made at such low energies. Furthermore, a resonance at 1.5 eV or below could not be observed in dissociative electron attachment experiments\(^{10}\) because the thresholds for formation of F\(^-\) + CF and CF\(^-\) + F are both above 1.9 eV.

In work related to the present study, electron attachment to CF\(_3\) radicals has been investigated between 300 and 600 K with the same modified flowing afterglow Langmuir probe experiment used here.\(^{13}\) In that work, formation of F\(^-\) in dissociative electron attachment was observed along with formation of CF\(_3\) anions in associative attachment; the ratio of these two channels depended strongly on the temperature and pressure of the gas. The temperature and pressure dependence of the measurements was fitted well with a kinetic modeling approach.\(^{13}\)

II. EXPERIMENT

Electron attachment to C\(_2\)F\(_3\) has been investigated with two complimentary experiments. At the Air Force Research Laboratory (AFRL), electron attachment has been studied with a new flowing afterglow Langmuir probe (FALP) technique that enables electron attachment to radicals to be observed in an inert bath gas at different temperatures. In Belfast, electron attachment to C\(_2\)F\(_3\) has been investigated under single collision conditions at different electron energies in the “Electron Radical Interaction Chamber” (ERIC), which has been described previously.\(^{14}\) Briefly, in ERIC a trochiodal electron monochromator (TEM) provides low energy electrons which interact with sample molecules in the source region of a small linear time-of-flight (TOF) mass spectrometer. The electron beam is pulsed; when all electrons have left the source region product ions are extracted into the drift tube of the time-of-flight mass spectrometer. The mass spectrometer potentials and extraction fields can be reversed so that either positively charged or negatively charged ions can be observed. The uncertainty in the electron energy scale is estimated to be \(\pm 0.2\) eV. The electron energy resolution is \(\sim 200\) meV, measured from the full width half maximum (FWHM) of the SF\(_6\) peak at 0 eV. The mass resolution of the mass spectrometer (FWHM \(M/\Delta M\)) is typically from 100 to 200.

The sample gas enters the spectrometer, ERIC, through a glass inlet system, which includes an Evenson microwave cavity. In the present investigation, C\(_2\)F\(_3\) was generated in the reaction of H atoms with C\(_2\)F\(_3\)I;

\[
C_2F_3I + H \rightarrow HI + C_2F_3
\]

The H atoms were generated in a He/H\(_2\) plasma generated by 60 to 100 W of 2.45 GHz radiation inside the Evenson cavity. The plasma region is separated by about 25 cm of glass tube from the interaction region. Downstream of the plasma and at a variable distance of 4–8 cm from the interaction region C\(_2\)F\(_3\)I was introduced to the gas flow. A similar method was used previously to prepare a sample of CF\(_2\) through a two step reaction of CF\(_3\)I with H atoms; in the first step CF\(_3\) was formed which rapidly reacts with a second H atom to give CF\(_2\) + HF.\(^{10}\)

At AFRL, a new flowing afterglow Langmuir probe (FALP) technique, dubbed variable electron and neutral density attachment mass spectrometry (VENDAMS), has recently been developed.\(^{15}\) VENDAMS allows for measurements of attachment to short lived species, such as radicals, and a variety of information on ion-ion mutual neutralization kinetics.\(^{16-19}\) The technique has been described in detail previously\(^{15,17}\) and only the aspects important to the present experiments are described here. A primarily Ar\(^+\)/e\(^-\) plasma is formed by a microwave discharge in pure He with Ar added downstream at 4% of the He flow rate to convert He\(^+\) and He metastables to Ar\(^+\). Approximately 5% of the positive ions are He\(^+\) and no negative ions are present except for very small impurity signals, e.g., Cl\(^-\). In these experiments C\(_2\)F\(_3\) was added through a neutral injector well after the plasma had been formed. The neutral is added in a known concentration of typically about \(3 \times 10^9\) cm\(^{-3}\) using a mass flow meter. These concentrations are achieved by using dilute mixtures;\(^{15}\) here, a 0.1% C\(_2\)F\(_3\)I in He mixture was used with flows of around 2 std. cm\(^3\) min\(^{-1}\). Chemistry initiated by electron attachment to C\(_2\)F\(_3\)I was allowed to proceed for 4.6 ms before the flowing gas encountered a sampling orifice to a quadrupole mass spectrometer with an analog multiplier. The entire flow tube is surrounded by resistance heaters and insulation in three zones for temperature variation. A moveable Langmuir probe is used to measure both the electron density along the flow tube axis and the plasma velocity. The latter is determined by pulsing the microwave discharge and noting the arrival time at the probe as a function of distance along the flow tube. The helium buffer density was \(3.2 \times 10^{16}\) cm\(^{-3}\) (1 Torr at 300 K) at all temperatures.

The primary data in a VENDAMS measurement are relative anion branching abundances present after the known reaction time as a function of the electron density at the reactant injector, [e\(^-\)]\(_0\). The electron density is varied by a combination of moving the microwave discharge position, changing the fraction of the helium that enters the cavity region, while adjusting a complimentary downstream He flow in order to maintain a constant number density, and by adjusting the power of the microwave discharge. Achievable [e\(^-\)]\(_0\) values range from below \(1 \times 10^{10}\) to \(5 \times 10^{10}\) cm\(^{-3}\).

At low [e\(^-\)]\(_0\) the only significant chemistry that occurred after introduction of C\(_2\)F\(_3\)I was the primary electron attachment,

\[
C_2F_3I + e^- \rightarrow I^- + C_2F_5.
\]

We have measured the attachment rate constants for this reaction in the traditional manner, i.e., by monitoring the electron concentration as a function of distance down the flow tube, for [e\(^-\)]\(_0\) low enough (\(\leq 10^9\) cm\(^{-3}\)) that other processes are negligible.\(^{20}\) Measurement of the plasma velocity provides the time scale for reaction. Reaction time profiles of the electron density were measured with and without the C\(_2\)F\(_3\)I added. The latter gave the diffusion rate, which tended to account for 10%–25% of the loss in electron density relative
to that lost to attachment. It is then straightforward to derive the rate constant for reaction (4).

Because every primary attachment produced a C$_2$F$_5$ radical, reaction (4) yielded a known concentration of C$_2$F$_5$ equal to the concentration of I$^-$. As [e$^-$]$_0$ was raised above the neutral concentration, electrons also attached to C$_2$F$_5$ to produce F$^-$ in measurable quantities,

$$C_2F_5 + e^- \rightarrow F^- + C_2F_4.$$  \hspace{1cm} (5)

Because both anions (I$^-$ and F$^-$) are atomic, as is Ar$^+$, mutual neutralization did not occur to any measurable extent, and no further chemistry needs to be considered. The concentration of cations produced through charge transfer from Ar$^+$ are far too low to measurably deplete the anion concentrations because of the low neutral concentration. The ratio of I$^-$ to F$^-$ is highly correlated with the ratio of the two rate constants for reactions (4) and (5).

The final piece of information needed to derive the rate constant for reaction (5) is the mass discrimination factor between F$^-$ and I$^-$ of the mass spectrometer. This discrimination factor was obtained by addition of NF$_3$ along with Ar to convert all electrons to F$^-$ ions. C$_2$F$_5$I was added downstream to convert quantitatively the F$^-$ to I$^-$,

$$F^- + C_2F_5I \rightarrow I^- + C_2F_6.$$  \hspace{1cm} (6)

Comparison of the loss of F$^-$ signal to the gain in I$^-$ signal as a function of the C$_2$F$_5$I flow yields the mass discrimination factor; for the current work this factor was 1.1 against I$^-$. In other cases, we have compared the discrimination factors determined with this method to those determined through a separate method of introducing two gases that deplete the e$^-$ density the same amount at a fixed Langmuir probe position downstream. The two methods have given identical results within our uncertainty.$^{15}$

III. RESULTS

A. Electron beam measurements

In Belfast, the presence of C$_2$F$_5$ radicals in the sample gas stream was confirmed by the measurement of positive ion mass spectra with varying electron energy. Figure 1 shows two-dimensional positive ion mass spectra where ion intensity is plotted as a function of ion time-of-flight on the abscissa and electron energy on the ordinate; spectra are shown with (a) plasma off and (b) plasma on. The positive ion mass spectra are not straightforward to interpret because C$_2$F$_5$I$^+$ is observed as a fragment from the ionization of C$_2$F$_5$I as well as from ionization of C$_2$F$_5$. Figures 2(a) and 2(b) show integrated signals of C$_2$F$_5$I$^+$, C$_2$F$_5$+$^+$, and HI$^+$ with the plasma off and on in the threshold region; these plots have been used to determine the appearance energies of these ions with the plasma on and off. The energy scale is calibrated to the ionization threshold of HI, 10.386 $\pm$ 0.001 eV.$^{23}$ From Figure 2(a) the appearance energy of C$_2$F$_5$I$^+$ is determined as 10.45 $\pm$ 0.15 eV. This energy is in agreement with previous determinations of the ionization energy of C$_2$F$_5$I; 10.67 eV,$^{24}$ 10.44 eV,$^{25}$ and 10.7 $\pm$ 0.1 eV.$^{26}$

In Fig. 2(b) integrated C$_2$F$_5$+$^+$ signals are shown with the plasma on and off. With the plasma off C$_2$F$_5$+$^+$ is formed in dissociative ionization of C$_2$F$_5$I and an appearance energy of 11.15 $\pm$ 0.15 eV is observed here, which agrees favourably with previously determined values; 11.1 $\pm$ 0.2 eV.$^{25}$

![FIG. 1. Two-dimensional plots of positive ion signal as a function of time-of-flight and electron energy with (a) plasma off and (b) plasma on.](image1)

![FIG. 2. Integrated positive ion signals (a) HI$^+$ and C$_2$F$_5$I$^+$ and (b) C$_2$F$_5$+$^+$ as a function of electron energy with plasma on and off.](image2)
There is also a very weak peak at 6 eV due to CF$_3$ in the spectrum with the plasma off and two faint peaks at 0 eV and 1.5 eV, which appears as a band centred at 4000 ns time-of-flight and electron energy with (a) plasma off and (b) plasma on. This noise has been seen before in spectra of fluorine containing molecules which appears as a small island just above 2000 ns time-of-flight. This noise has a primary negative ions formed are F$^-$ and I$^-$.

The clear difference between the two data sets is that with the plasma on there is a new F$^-$ peak at 0 eV. The two spectra both have some broad noise around zero eV electron energy, which appears as a band centred at 4000 ns time-of-flight and a small island just above 2000 ns time-of-flight. This noise has been seen before in spectra of fluorine containing molecules and appears to be linked to collisions with grids in the time-of-flight mass spectrometer. There is a little background noise visible in Figure 3(b) with the plasma on across the spectrum, and appears to be linked to collisions with grids in the time-of-flight mass spectrometer.

Figure 3 shows two-dimensional spectra of negative ions formed in electron attachment with (a) the plasma off and (b) plasma on recorded under identical conditions to the positive ion spectra. An initial inspection of the data shows that in both spectra the primary negative ions formed are F$^-$ and I$^-$.

The appearance energy of C$_2$F$_5$ is 3 orders of magnitude or more. The noise level is lower with the plasma on the number density of C$_2$F$_5$I is reduced and this signal is too weak to be seen.

With the plasma on, C$_2$F$_5$ and HI are also present in the gas stream. HI makes a contribution to the I$^-$ signal at 0 eV in Figure 4(b), but HI does not contribute to the I$^-$ signal between 1 and 4 eV. The F$^-$ signal in Figure 4(d) has contributions from C$_2$F$_5$ and C$_2$F$_5$I. The contribution of C$_2$F$_5$I to the F$^-$ signal in Figure 4(d) has been removed with the following method. First, the fraction of C$_2$F$_5$I remaining in the gas stream. HI makes a contribution to the I$^-$ signal at 0 eV in Figure 4(b), but HI does not contribute to the I$^-$ signal between 1 and 4 eV. The F$^-$ signal in Figure 4(d) has contributions from C$_2$F$_5$ and C$_2$F$_5$I. The contribution of C$_2$F$_5$I to the F$^-$ signal in Figure 4(d) has been removed with the following method. First, the fraction of C$_2$F$_5$I remaining in the gas stream.

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sample with the plasma on was determined by careful comparison of the total \( I^- \) signal from \( \text{C}_2\text{F}_5\text{I} \) between 1 and 4 eV with the plasma off and on shown in Figures 4(a) and 4(b). Second, the \( \text{F}^- \) spectrum from \( \text{C}_2\text{F}_5\text{I} \) with the plasma off in Figure 4(c) was multiplied by this fraction and subtracted from the \( \text{F}^- \) spectrum taken with the plasma on, shown in Figure 4(d), to give the \( \text{F}^- \) spectrum shown in Figure 4(e) which represents the \( \text{F}^- \) ions formed in dissociative electron attachment to \( \text{C}_2\text{F}_5\text{I} \) only. No adjustable parameters were used in this subtraction procedure. It is clear that in the region between 1 and 4 eV electron energy in Figure 4(e) the \( \text{F}^- \) signal is zero after the contribution due to \( \text{C}_2\text{F}_5\text{I} \) is removed within the experimental uncertainty; the error bars shown indicate uncertainties of \( \pm 1 \) standard deviation and all random uncertainties have been taken into account, including the uncertainty in the fraction of \( \text{C}_2\text{F}_5\text{I} \) present with the plasma on.

The \( \text{F}^- \) spectrum due to electron attachment to \( \text{C}_2\text{F}_5\), shown in Figure 4(e), has a strong peak at 0 eV, but has no other clear features. The uncertainty in the spectrum, however, may well hide the formation of negative ions in other dissociative electron attachment processes at higher energy, particularly between 1 and 4 eV.

### B. VENDAMS data

The \( \text{C}_2\text{F}_5\text{I} \) attachment rate constant, reaction (4), was determined at each temperature in the normal FALP fashion, as described above.\(^{20} \) Examples of such data are plentiful in the literature and are not shown here.\(^{30, 31} \) Table I shows the rate constants at various temperatures for both reactions (4) and (5) measured in the present work. Electron attachment to \( \text{C}_2\text{F}_5\text{I} \) is exothermic by 0.79 eV.\(^{25} \) The rates of attachment to \( \text{C}_2\text{F}_5\text{I} \) are rapid; we estimate that it occurs in about 50% of collisions. There is a negative temperature dependence, indicative of an efficient \( s \)-wave process.\(^ {32, 33} \) An unpublished rate constant has been referenced\(^{25} \) for electron attachment to \( \text{C}_2\text{F}_5\text{I} \) of \( 2 \times 10^{-8} \) cm\(^3\) s\(^{-1}\) at 300 K due to Sungawa and co-workers.\(^{19, 34–37} \) That value is incompatible with the present measurements.

Raw VENDAMS data at 500 K, corrected for mass discrimination, are shown in Figure 5. At low \([e^-]_0\), \( I^- \) is essentially the only negative ion present, with just 0.2% of the signal observed as \( \text{F}^- \). As \([e^-]_0\) increases, the fraction of \( \text{F}^- \) increases substantially such that it is 7% of the signal at the highest density measured. Data at other temperatures are qualitatively identical. The rate constant for reaction (5), electron attachment to \( \text{C}_2\text{F}_5\), is derived from the VENDAMS data by modeling the kinetics of all reactions occurring in the flow tube and fitting to the observed anion abundances. Experimental conditions are chosen such that only the fastest reactions amongst the species present in the highest concentrations can have any measurable effect on the anion abundances. For this study, the chemistry is extremely simple and only electron attachment to \( \text{C}_2\text{F}_5\text{I} \) and \( \text{C}_2\text{F}_5\), reactions (4) and (5), as well as diffusion, affect the comparison of model to data. Other reactions are included in the modeling for completeness, however, ion-molecule reactions are two orders of magnitude slower than the primary attachment and do not play a role at the very low \( \text{C}_2\text{F}_5\text{I} \) densities used in VENDAMS experiments.\(^{38} \) Derivation of the rate constant of reaction (5) along with uncertainty limits employs a Monte Carlo technique as follows: (1) rate constants for all reactions are randomly chosen within limits set by either a calculated collision rate or literature values where known; (2) assuming that set of rate constants, the anion abundances at the end of the 4.6 ms reaction time are calculated by iteratively solving the set of coupled differential equations describing the reaction system; (3) the calculated abundances are compared to the experimental values via a weighted least squares goodness of fit (zero being a perfect fit); (4) rate constants are varied through a simple, downhill optimization to find a local minimum in the goodness of fit; (5) the process is continuously repeated from new initial random guesses, finding other local minima until the full parameter space has been explored. For the current simple system this requires only \( 10^2–10^3 \) initial guesses and tens of seconds of computation on a desktop computer. Best fit and uncertainty limit values are determined from plots of the goodness-of-fit parameter as a function of the rate constant under consideration. Figure 6 shows a goodness-of-fit plot for the data in Figure 5 for the rate constant for electron attachment to \( \text{C}_2\text{F}_5\), reaction (5). The solid line in Figure 5 represents the fit using the best fit value, \( 4.4 \times 10^{-9} \) cm\(^3\) s\(^{-1}\); the data are reproduced extremely well. Error limits are determined by the extreme values of the rate constant at the goodness-of-fit corresponding to fits that, as

![FIG. 5. VENDAMS experimental (points) and best-fit calculated (solid lines) anion abundances as a function of initial electron density 4.6 ms after addition of \( 3.8 \times 10^9 \) cm\(^{-3}\) \( \text{C}_2\text{F}_5\text{I} \) to the afterglow at 500 K. Dashed lines are the calculated abundances at the uncertainty limits of \( r m k_{\text{C}_2\text{F}_5\text{I}+e^-}. \)](image)

### Table I. Rate constants as a function of temperature for reactions (4) and (5).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( \text{e}^- + \text{C}_2\text{F}_5\text{I} ) (( \pm 25% ))</th>
<th>( \text{e}^- + \text{C}_2\text{F}_5 ) (( \pm 35% ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>( 1.5 \times 10^{-7} )</td>
<td>( 3.7 \times 10^{-9} )</td>
</tr>
<tr>
<td>400</td>
<td>( 1.5 \times 10^{-7} )</td>
<td>( 3.8 \times 10^{-9} )</td>
</tr>
<tr>
<td>500</td>
<td>( 1.4 \times 10^{-7} )</td>
<td>( 4.4 \times 10^{-9} )</td>
</tr>
<tr>
<td>600</td>
<td>( 1.1 \times 10^{-7} )</td>
<td>( 4.5 \times 10^{-9} )</td>
</tr>
</tbody>
</table>
determined by eye, clearly no longer reproduce the data. In the example shown in Figure 6 a goodness-of-fit of 1 has been chosen as the maximum allowable value. The shaded area in Figure 6 then represents acceptable fits. Error limits are determined by the extremes at a goodness-of-fit of 1 and the fits to those values are shown as dashed lines in Figure 5. The uncertainty in the C2F5I rate constant measurement is not fully propagated to the derivation of the C2F5 rate constant because the latter is largely a function of the relative, not absolute, abundances of I− and F−. A more in-depth description of the analysis can be found in Ref. 39.

The C2F5 attachment rate is almost two orders of magnitude slower than the C2F5I rate and increases 20% as the temperature rises from 300 to 600 K. This change, however, is well within the experimental uncertainty. The variation of rate constant with temperature can be seen in Figure 7.

IV. DISCUSSION

In previous experiments in Belfast it has been possible to make an estimate of the absolute electron attachment cross section for highly reactive molecules, such as CS,40 by making an estimate of the target molecule number density in the interaction region. Previous estimates, however, have been made at electron energies significantly above 0 eV, e.g., 4–6 eV in the case of CS. Here, however, there is an additional challenge because dissociative electron attachment to C2F5 occurs so close to zero energy where cross sections generally change quite dramatically over a small energy range; the experimental electron beam resolution is not sufficient to resolve the peak shape close to zero in the present work. With an electron beam resolution of ~20 μeV it has been experimentally demonstrated for SF6 that from <10 μeV to ~10 meV the s-wave electron attachment cross section, σ, follows the theoretically predicted σ ∝ E−1/2 form.41 Thus, s-wave attachment cross sections rise as the energy decreases to theoretically infinite values at zero energy. By contrast, it has also been observed experimentally, in dissociative electron attachment to Cl2, that from ~1 to 50 meV the p-wave attachment cross section follows the theoretically predicted σ ∝ E1/2 form.42 Thus, p-wave attachment cross sections drop to zero at zero energy. Therefore, it has not been possible with the electron beam data to estimate an absolute cross section for electron attachment to C2F5, but it has been possible with the VENDAMS data to determine rate constants at different temperatures.

Electron attachment in the multiple collision conditions of the FALP experiment can be viewed as a series of these fundamental processes:

\[
\text{C}_2\text{F}_5 + e^- \xrightarrow{k_{at}} \text{C}_2\text{F}_5^{-\ast} \tag{7}
\]

\[
\text{C}_2\text{F}_5^{-\ast} \xrightarrow{k_{det}} \text{C}_2\text{F}_5 + e^- \tag{8}
\]

\[
\text{C}_2\text{F}_5^{-\ast} + M \xrightarrow{k_{rat}} \text{C}_2\text{F}_5^{-} + M \tag{9}
\]

\[
\text{C}_2\text{F}_5^{-} \xrightarrow{k_{dist}} \text{C}_2\text{F}_4 + F^- \tag{10}
\]

After electron capture, process (7), the excess energy of the superexcited C2F5− anion must be disposed of through one of the competing processes (8)–(10). The measured rate constants of dissociative electron attachment to C2F5, reaction (5), are fairly slow; only about 1 in 100 collisions results in dissociative electron attachment.32 These rate constants depend, of course, on the rates of the individual processes (7)–(10). The collisional stabilization process, (9), can be discounted in the present case as no trace of stable parent ion C2F5 was observed in the VENDAMS experiment. Therefore, there are two extreme cases that can explain why only 1 in 100 collisions leads to dissociative electron attachment. In the first scenario the electron attachment is rapid and occurs at the collisional rate, but the rate of electron detachment, process (8), is ~100 times faster than dissociation, process (10). The other extreme situation would be where the rate of electron attachment is ~100 times slower than the collisional rate, but dissociation, process (10), is significantly greater than the
rate of detachment, process (8). Alternatively, there might be a situation somewhere between these two extremes.

Recently, a new method of kinetic modeling for analyzing thermal electron attachment systems has been developed by Troe and co-workers. This method requires fitting several adjustable parameters to the data. By assuming that attachment leads to formation of a vibrationally excited $\text{C}_2 \text{F}_5^-$ anion in its electronic ground state, the kinetic modeling can be applied here. Briefly, collision rate constants are calculated using extended Vogt-Wannier theory. Both the attachment rate constant (7) and the resulting energy distribution of $\text{C}_2 \text{F}_5^-$ are calculated using an empirical factor to account for inefficiency of capturing higher energy electrons beyond the limit set by extended Vogt-Wannier theory. This increased inefficiency may be due either to the rate of intramolecular vibrational energy redistribution i.e., the incorporation of the electron and its energy into the molecule via electron-phonon coupling) or from competition by electron scattering. Autodetachment (8) and dissociation (10) specific rate curves are calculated using statistical theory by employing microscopic reversibility of (7) and by employing the simplified statistical adiabatic channel model. Finally, competition between (8)–(10) is determined by explicitly accounting for collisions with the buffer gas and approximating the solution to the Master Equation using the many-shots approach.

As determined with the kinetic modeling, neither stabilization of $\text{C}_2 \text{F}_5^-$ through collisions with the buffer gas, process (9), nor autodetachment (8) occur quickly enough to compete with the dissociation, process (10). The failure of (9) to compete is consistent with no parent anion signal being observed and not surprising as dissociative electron attachment is exothermic by 0.5 eV, as calculated with GAUSSIAN-3 (G3) theory. The calculated unimolecular rate constant for autodetachment is on the order of 100 s$^{-1}$ at threshold, while that of dissociation is, even under generous assumptions, $>10^7$ s$^{-1}$ at the same energy. The rate of autodetachment increases more rapidly with energy, but reaches only $\sim10^4$ s$^{-1}$ at 0.4 eV above threshold, at which point the thermal distribution is negligible. Because autodetachment never competes effectively with dissociation, the low attachment rate constants must be due to the second extreme case presented above where the rate of electron attachment (7) occurs at only 1/100th of the maximum value.

Many thermal electron attachment processes show Arrhenius behaviour over moderate temperature ranges. The $\text{C}_2 \text{F}_3$ data may be fitted to an Arrhenius equation assuming a small activation energy of 90 cm$^{-1}$; corresponding to an energetic barrier between the neutral and anion potential energy surfaces where some amount of vibrational excitation is needed to surmount the barrier. The Arrhenius description tends to fail at higher energies and offers limited physical insight into the magnitude of the rate constants. Invoking the kinetic modeling approach instead, the $\text{C}_2 \text{F}_3$ data are well fit between 300 K and 600 K by assuming purely s-wave attachment, a somewhat larger barrier of 560 ± 200 cm$^{-1}$, and a significant decrease in capture efficiency of higher energy electrons from that calculated using Vogt-Wannier theory. In the language of the kinetic model, $c_1 = 20$ assuming the electron capture probability as a function of collision energy falls as $e^{-\kappa e^2}$, where $\kappa$ is proportional to the square root of the collision energy. The best fit $c_1$ value corresponds to a FWHM of the zero-energy peak in Figure 4(e) of 0.015 eV, much less than the upper limit of 0.2 eV set by the experimental resolution of the beam measurements; the 0.2 eV FWHM sets a lower limit on $c_1$ of 4. The modeling suggests a larger barrier than does an Arrhenius fit; interestingly, application of R-matrix theory to other exothermic dissociative electron attachments also suggests that Arrhenius underestimates the barrier height in such systems.

The near flat temperature dependence of the rate constant over the measured range is the result of the positive dependence on the $\text{C}_2 \text{F}_5$ internal energy distribution being offset by the negative dependence on the electron temperature. At lower temperatures, the former will dominate, and Arrhenius fit behaviour is predicted. At higher temperatures or for non-thermal plasmas, the latter will dominate and, in the absence any higher energy resonances as indicated by the beam measurements, a steep negative temperature dependence is predicted. Extrapolated attachment rate constants derived from the kinetic modeling are shown in Figure 7. Uncertainty in the extrapolated values increases at conditions far from the experiment to up to an order of magnitude; however, the qualitative trends shown may be considered robust. The temperature dependence is very similar to that of attachment to $\text{CF}_3$. Although not measured, it is expected that due to the rapid dissociation rate of $\text{C}_2 \text{F}_5^-$ that the electron attachment rate constant will not have any pressure dependence even up to atmospheric pressures, which is very different to $\text{CF}_3$, where non-dissociative attachment occurs and there is a measurable positive pressure dependence at pressures on the order of 1 Torr. This difference stems primarily from the fact that dissociative attachment to $\text{CF}_3$ is slightly endothermic, while dissociative attachment to $\text{C}_2 \text{F}_3$ is exothermic.

The observation of an anion peak close to zero electron energy is due in some cases to dissociative electron attachment to vibrationally excited molecules, rather than to molecules in the ground vibrational state. Electron attachment to vibrationally excited $\text{SF}_6$ molecules, for example, can lead to the observation of a peak close to zero electron energy of $\text{SF}_2$ fragment ions, which is not observed in electron attachment to ground state $\text{SF}_6$ molecules. The flat temperature dependence of the $\text{F}^-$ formation rate constant indicates that there is no such dramatic dependence on the initial vibrational state in dissociative electron attachment to $\text{C}_2 \text{F}_5$.

V. CONCLUSIONS

In this work the observation formation of $\text{F}^-$ in dissociative electron attachment to $\text{C}_2 \text{F}_3$ close to zero eV electron energy has been observed independently in two different experiments; a single collision beam experiment in Belfast and a multiple collision experiment with a buffer gas at AFRL. It has not been possible to measure absolute cross sections with the beam experiment, but the rate constant of electron attachment to $\text{C}_2 \text{F}_3$ has been measured at AFRL. The rate constant appears to increase slightly as the temperature is raised. Rate constants measured correspond to $\sim1$ dissociative electron
attachment event per 100 collisions, which appears to be due to inefficient capture of low energy electrons by C$_2$F$_5$.

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