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Contract 61775-02-C4032; Final Report
Period: 20050216 - 20050615

This report covers the final period of contract 61775-02-C4032. Thus, finalizing projects rather than starting new ones has characterized the period. No experiments have been conducted at CRYRING

Three papers have been published during the period. First, the paper on $C_3D_7^+$ and $C_4D_9^+$ was published in Journal of Chemical Physics [1]. The study of $C_3D_7^+$ represents the most detailed in terms of product branching ratios for a molecular ion of this complexity. For $C_4D_9^+$ we could only determine the C–C bond breaking, which was found to be 39%.
In the previous report we mentioned briefly that we had new data on dissociative recombination of CO_2^+. In particular, we did not find, as opposed to a report from the ASTRID storage ring, that the $C + O_2$ has a non-zero branching ratio. We allowed our data to be reviewed by the ASTRID team. A possible explanation for the discrepancy between the two storage rings could be an incorrect background subtraction in the treatment of the ASTRID data. We find that the branching ratio for the CO + O channel is 100 %. The ASTRID data have already been included into models of the atmospheres of Venus and Mars, where the dissociative recombination of CO_2^+ is considered to be a major source of C. The results from CRYRING show that this conjecture is incorrect [2].

The CF^+ ion is important to the modeling of the chemistry of fluorocarbon plasmas. The dissociative recombination of this ion was studied both in CRYRING and ASTRID. The experiments were complimentary in the respect that absolute cross sections were measured at CRYRING but not ASTRID, and relative cross sections were measured over a broader energy range in ASTRID as compared with CRYRING. We found the rate constant for dissociative recombination to be strikingly low, only about 5×10^{-8} cm^3s^{-1}, which is lower than the few times 10^{-7} cm^3s^{-1} usually found for non-hydride diatomics. This is puzzling since the ground state of CF^+ is crossed by neutral states, which is usually sufficient to effectively drive dissociative recombination [3].

The analysis of the branching ratios for CF_2^+ has been completed. We are considering a joint paper with the ASTRID team, who has data for CF_3^+, but so far this publication has not been finalized.
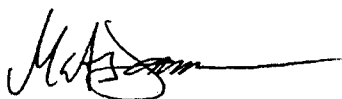
Finally, A. Ehlerding, whose PhD student position is financed by the contract, spent one month together with A.A. Viggiano's group at Hanscom. The Selected Ion Flow Tube (SIFT) was used to study reactions with NO_3^- with SO_2. The experiment was successful and a publication is being prepared.

Since the last report, the following papers have appeared in print:

1. M. Larsson, A. Ehlerding, W.G. Geppert, F. Hellberg, S. Kalhori, R.D. Thomas, N. Djuric, F. Österdahl, G. Angelova, J. Semaniak, O. Novotny, S.T. Arnold, and A.A. Viggiano, "Rate constants and branching ratios for the dissociative recombination of $C_3D_7^+$ and $C_4D_9^+$", *J. Chem. Phys.* **122**, 156101 (2005).

2. A.A. Viggiano, A. Ehlerding, F. Hellberg, R.D. Thomas, V. Zhaunerchyk, W.D. Geppert, M. Kaminska, and F. Österdahl, "Rate constants and branching ratios for the dissociative recombination of CO_2^+", *J. Chem. Phys.* **122**, 226101 (2005).

3. O. Novotny, J.B.A. Mitchell, J.L. LeGarrec, A.I. Florescu-Mitchell, C. Rebrion-Rowe, A. Svendsen, M.A. El Ghazalay, L.H. Andersen, A. Ehlerding, A.A. Viggiano, F. Hellberg, R.D. Thomas, V. Zhaurenechyk, W.D. Geppert, H. Montaigne, M. Kaminska, F. Österdah, and M. Larsson, "The dissociative recombination of fluorocarbon ions: I. CF^+", *J. Phys. B* **38**, 1471 (2005).

Sincerely,

Mats Larsson

REPORT DOCUMENTATION PAGE

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

This report results from a contract tasking Stockholm University as follows: CRYRING, a synchrotron/heavy-ion storage ring facility, has proved to be a powerful tool for measurements of branching ratios in recombination of polyatomic molecular ions. However, there are important questions that still need to be addressed for organic ions such as: 1) Is there a mass limit at which fragmentation decreases or even vanishes and most or all of the electron energy is converted to internal degrees of freedom? 2) What is the order, n, of the dissociation shown in reaction? 3) Is the fragmentation process instantaneous? Or is there a delay in the break-up process? For a small inorganic ion such as H_2O^+ the break-up process is most likely instantaneous, but whether this is also true for larger organic ions is unknown. 4) Is the break-up process a one-step or a multi-step process? Prediction of the products of dissociative recombination is very difficult. It is here proposed to study not only the rates of dissociative recombination of ions important for plasma-enhanced combustion but also the neutral product distributions. Experiments with many important hydrocarbon ions (the benzene cation, for example) will be performed. Another problem concerns the resolution of the solid-state particle detector, because well-resolved mass peaks facilitate the measurement of product branching ratios. Deuterated molecules and peak fitting procedures will be applied to enhance the resolution. The proposed measurements will add greatly to the knowledge base in this unexplored field, yielding answers to the questions outlined above and serving as important inputs to the Air Force combustion models.

15. SUBJECT TERMS
EOARD, Physics, Plasma Physics, Combustion, Inorganic Chemistry, Molecular Chemistry

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The dissociative recombination of fluorocarbon ions: II. CF⁺

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Abstract
The dissociative recombination and excitation of CF⁺ have been measured at the
ASTRID and CRYRING storage rings. Though examination of the available
potential energy curves would suggest that the recombination rate would be
large for this ion, in fact a rate constant of $5.2 \pm 1.0 \times 10^{-8} (T_e/300)^{-0.8} \text{ cm}^3 \text{ s}^{-1}$
was found. The recombination cross section at low energies falls off to a
minimum at 0.5 eV centre-of-mass collision energy but exhibits resonances
at energies above this. The dissociative excitation cross section leading to
C⁺ + F was also measured and this displays an onset beginning at about 7 eV.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Fluorocarbon radicals and ions are observed in fluorocarbon plasmas used for semiconductor
processing and in flames following the introduction of fluorinated extinguishing agents. In
a previous publication [1] (hereafter paper I in this series), we have reported a measurement
of the rate coefficient for the dissociative recombination of CF₃⁺, performed using a flowing
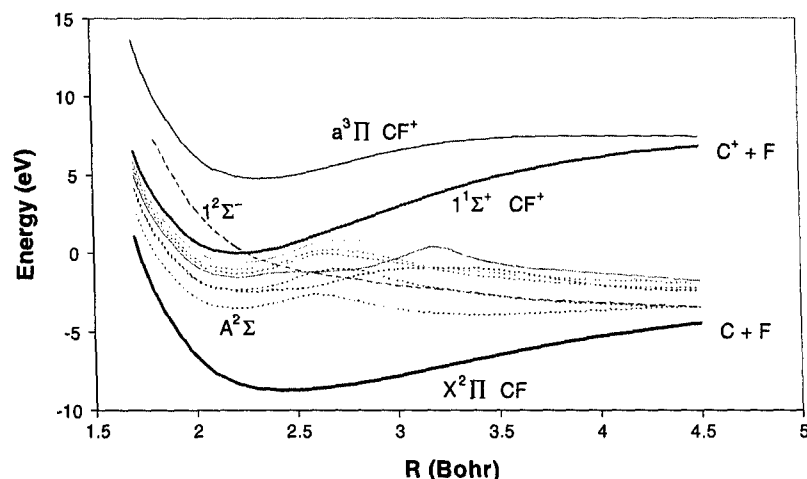afterglow Langmuir probe–mass spectrometer (FALP–MS) apparatus. In this second paper,

Figure 1. Adiabatic potential energy curves of the ground and excited states of CF and CF^+ [3]. The lower thick solid (blue curve) is the $X^2\Pi$ state of CF and the upper thick solid (red) curve, the $X^1\Sigma^+$ state of CF^+. The dotted curves are excited Π and Σ states of CF while the thin solid (purple) curve, lying above the ground state of CF^+, shows the $a^3\Pi$ state of the ion [4].

we have used the ASTRID and CRYRING heavy-ion storage rings and electron coolers at the University of Aarhus, Denmark, and the University of Stockholm, Sweden, to perform merged beam studies of electron–CF^+ collisions. The spectroscopy of the CF radical has been studied by a number of authors [2] (and references therein) and the potential energy curves for CF and CF^+ have been calculated [2–5]. Examination of these curves, some of which are shown in figure 1, indicates a rich structure in the excited states of the neutral. There are a number of avoided curve crossings below the ion state since the crossing of adiabatic curves with the same symmetry is forbidden by the Wigner non-crossing rule [6]. In a diabatic picture, such states can cross and so from the figure, one would expect that there should be a number of neutral states crossing the ion in the vicinity of the ground vibrational level. Therefore, it might be predicted that the recombination cross section via the direct mechanism would be large. It should be noted that the $1^1\Sigma^-$ state cuts through the $1^1\Sigma^+$ ion ground state (these states having different symmetry) but transitions between such states are forbidden [7] and so this will not participate in the recombination process.

The ion–molecule reaction chemistry of CF^+ has been studied by Morris *et al* [8] and while they found that it reacts rapidly with CF_4, the plot of reactant ion signal versus neutral gas concentration was curved, indicating the presence of two states of the ion, one of which was non-reactive. Morris *et al* confirmed this finding by using NO as a monitor gas. The ionization potential (IP) of NO is 9.264 eV while that for CF is 9.11 eV and so the reaction of the ground state of CF^+ is endothermic by 0.15 eV in this case. CF^+ was found to react with NO thus indicating the presence of an excited ion state. By observing no reactions with O_2 and Xe, (IPs of 12.071 and 12.130 eV respectively) they were able to rule out the possibility that the reactive state was electronically excited. Through these and other reaction studies, they attributed the reactive CF^+ to be due to vibrationally excited states with the ground vibrational state being unreactive.

Langford *et al* [9] have reported the observation of an electronically excited $a^3\Pi$ state that lies between 3.4 and 4.8 eV above the ground state of CF^+ [4, 5]. In that study, the CF^+

Bending
Magnets

ASTRID

RF

Electron
cooler

Ion
Source

150 kV

Solid state
detector
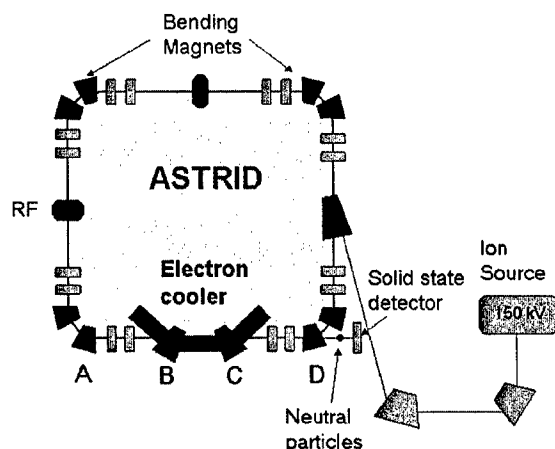
A   B   C   D

Neutral
particles

Figure 2. Layout of the ASTRID storage ring showing beam injection, electron cooler and neutral particles detection system. Magnets are labelled A–D.

ions were produced by electron impact on CF_4 while Morris *et al* used CF_3Br as the parent gas. Other authors [10–14] have also found the presence of excited CF^+ states when the ion is produced from a fluorocarbon precursor. Reid [14] was able to quantify the percentage of the $a^3\Pi$ state in a beam of CF^+ using a measurement of translational energy loss spectroscopy, where he studied the energy loss due to excitation of the CF^+ ions in the beam by collision with a target gas. He found that, when produced from CF_4, as much as 32% of the CF^+ ions were in this excited metastable state. This figure dropped to only 2% for ions derived from partially halogenated gases, confirming the findings of Morris *et al*. Since in the present study CF_4 was used as the parent gas, it must be assumed that the beam initially has a high proportion of the $a^3\Pi$ state. The lifetime of this state is believed to be short, however, and so it should decay during the acceleration and initial storage period, prior to the recombination measurement. Results discussed later support this latter statement.

2. Experimental method

The experiment was performed using the electron–ion merged beams technique at the heavy-ion storage rings ASTRID at the University of Aarhus, Denmark, and CRYRING at the University of Stockholm, Sweden. At ASTRID, the ions under study were produced from tetrafluoromethane (CF_4) in an electron impact source at 1 mTorr, accelerated to 150 keV and injected into the storage ring (shown in figure 2) where they were further accelerated to 2.5 MeV. This process takes about 4 s to accomplish at ASTRID.

At CRYRING, the ions were produced using the same type of ion source also using CF_4 as the source gas. Instead of using the filament, the plasma was created by electrical discharge at 1 kV, at a pressure of about 0.1 Torr. The ions were extracted at 40 keV and injected into the ring where they were further accelerated to 3.1 MeV during 1 s. The beam lifetime was 1.2 s.

In both experiments, an electron beam of known energy, formed in the electron cooler assemblies, was merged with and de-merged from the ions in the storage ring using toroidal magnets (like B and C shown in the figure). At ASTRID, the electron beam had a longitudinal

temperature $kT_\parallel \sim 0.5$ meV and a transverse temperature $kT_\perp \sim 25$ meV. This value is obtained by the adiabatic expansion of the electron beam by means of a spatially increasing axial magnetic field in the cathode region. At CRYRING, the electron beam had a transverse temperature $kT_\perp \sim 2$ meV and a longitudinal temperature of $kT_\parallel \sim 0.1$ meV. The electron velocity is varied with respect to that of the ions so that a range of centre-of-mass collision energies can be achieved. More details concerning the ASTRID and CRYRING electron coolers are available in [15, 16].

At ASTRID, neutrals formed in the straight section between magnets A and D (figure 2) pass undeflected through magnet D and are detected by a surface-barrier detector located at a distance of 6 m from the exit of the electron cooler magnet C. There are two sources for these neutrals. One involves interaction of the stored ion beam with the background gas in the storage ring which is maintained at a pressure of about 10^{-11} Torr. The other source is the interaction of the ions with the electron beam. For low centre-of-mass collision energies, this interaction is only due to dissociative recombination. The electron beam is chopped on and off (at a frequency of 20 Hz) by modulating the bias voltage on the anode, and counts are accumulated separately with the electron beam off (background only) and with the beam on (background plus electron–ion recombination signals). The experimental rate coefficient $\langle v\sigma \rangle$ is derived from the difference in these signals using the equation

$$\langle v\sigma \rangle = \frac{N_s - N_b}{N_{ion}\, n_e}\, \frac{v_i}{\Delta L \varepsilon},\tag{1}$$

where v is the relative velocity, σ the recombination cross section, v_i the ion velocity, n_e the electron density, ΔL ($=0.95$ m) the length of the interaction region and ε ($=1$) the detection efficiency. N_s and N_b are the counting rates of neutrals recorded by the detector with the electron beam on and off, respectively, and N_{ion} is the number of ions passing through the electron cooler per second. At ASTRID, the ion beam current was too small to measure directly and a relative experimental rate was measured.

At CRYRING a similar measurement technique was used [17] but in this case the absolute ion current was measured using a secondary transformer method [18].

The rate coefficients were measured as a function of the centre-of-mass collision energy E_{cm} by varying the energy of the electron beam. If the reduced mass is approximated with the electron mass, E_{cm} is given by

$$E_{cm} = \frac{1}{2} m_e (v_i - v_e)^2 = \left[\sqrt{\frac{m_e}{m_i} E_i} - \sqrt{E_e} \right]^2,\tag{2}$$

where m_i and m_e are the ion and electron masses, and E_i and E_e are the ion and electron laboratory energies. A correction to the centre-of-mass energy must be applied to account for the merging and de-merging (toroidal) regions (B and C in figure 2) where the angle between the ion and electron beams is not zero. This means that the interaction energy is higher in these regions. This small correction is discussed in [17, 19, 20] and has the most effect in an energy interval such as that shown in figure 4 around 0.5 eV which is followed by a rise in the cross section at higher energies.

3. Estimation of the lifetime of the $a^3\Pi$ state

The $a^3\Pi \to X^1\Sigma^+$ transition is spin forbidden and its lifetime is given by the relation [21]

$$\frac{1}{\tau(a^3\Pi)} = \left(\frac{\langle a^3\Pi | H_{so} | A^1\Pi \rangle}{E(A^1\Pi) - E(a^3\Pi)} \right)^2 \times \left(\frac{v(a^3\Pi - X^1\Sigma^+)}{v(A^1\Pi - X^1\Sigma^+)} \right)^3 \frac{1}{\tau\, A^1\Pi}.\tag{3}$$

The off-diagonal spin–orbit matrix element can be approximated by the spin–orbit coupling constant $A(^3\Pi)$ as discussed in [22]. The difference $E(A^1\Pi) - E(a^3\Pi)$ is the energy gap between the $A^1\Pi$ and $a^3\Pi$ states whereas the $v(a^3\Pi-X^1\Sigma^+)$ and the $v(A^1\Pi-X^1\Sigma^+)$ denote the transition energies between the $a^3\Pi$ and the ground state and the $A^1\Pi$ state and the ground state. The radiative lifetime $\tau(A^1\Pi)$ is given in units of seconds by

$$\frac{1}{\tau(A^1\Pi)} = 2.026 \times 10^{-6} v^3(A^1\Pi - X^1\Sigma^+)\Delta R_e^2(A^1\Pi \rightarrow X^1\Sigma^+), \qquad (4)$$

where the transition energy $v(A^1\Pi-X^1\Sigma^+)$ is expressed in cm^{-1} and the internuclear separation at the bottom of the corresponding wells, ΔR_e, in Å. Values for these quantities are 68 223 cm^{-1} and 0.13 Å, respectively, from [4]. Hence the radiative lifetime of the $A^1\Pi$ state is found to be 90 ns.

The spin–orbit coupling constant for the ground state of CF^+ is calculated [23] to be 65.3 cm^{-1} and we can make the assumption that this will not change much for the $a^3\Pi$ state. From [4], $E(A^1\Pi)-E(a^3\Pi) = 28\,389$ cm^{-1}, $v(a^3\Pi-X^1\Sigma^+) = 39\,841$ cm^{-1} and $v(A^1\Pi-X^1\Sigma^+) = 68\,230$ cm^{-1}. With these figures, one obtains an estimated lifetime for the $a^3\Pi$ state of 0.086 s. This is long compared to typical measurement times in experiments such as that of Reid [14], discussed in the introduction but given in our experiment, the recombination measurement begins several seconds after the ion is formed, this state should have completely decayed in our apparatus.

4. Calculation of rovibrational state lifetimes

As discussed in the previous section, one of the essential features of the storage ring technique is that the ions circulate in the ring for several seconds before the actual electron–ion reactions are studied. They therefore have sufficient time for radiative cooling of vibrational states to occur if they are infrared active. This is not necessarily the case for rotationally excited states, and indeed recent studies have indicated often that the ions studied in storage ring experiments have been rotationally excited to more than the expected 300 K energy [24]. In the present experiments, preliminary analysis of imaging measurements of the energy release of the recombination products (to be published separately) indicates that the rotational temperature of the ions is about 6000 K. Given that the vibrational and rotational constants for CF^+ have been measured [25, 26] to be 1766 cm^{-1} and 1.72 cm^{-1} respectively, this implies that states with up to $v = 2$ or $J = 50$ would be populated. In order to characterize this more clearly, a calculation of the lifetimes of the rovibrational states of the $X^1\Sigma_g$ ground state and of the metastable $a^3\Pi$ states of CF^+ has been performed. For the evaluation of the CF^+ rovibrational lifetimes we followed a procedure similar to that presented in [27] by Amitay *et al*. The Einstein coefficients were evaluated as

$$A_{vJ'=J,J\pm1} = 3.12 \times 10^{-7} \times H(J' = J, J \pm 1, \Lambda) \sum_{v'=0}^{v} \Delta E_{vJ,v'J'=J,J\pm1}^3 |\langle\Psi_v|\mu(R)|\Psi_{v'}\rangle|^2,$$

$$(5)$$

where $H(J', \Lambda)$ takes account of the separation of rotational and vibrational motion and has different forms in the P $(J' = J - 1)$, Q $(J' = J)$ and R $(J' = J + 1)$ branches [27]. (For a discussion of the numerical factor see the appendix). The total Einstein coefficient is then

$$A_{vJ} = A_{vJ-1}^P + A_{vJ}^Q + A_{vJ+1}^R. \qquad (6)$$

Table 1. Lifetimes, in seconds, of the vibrational levels of the $X^1\Sigma^+$ and $a^3\Pi$ states of CF^+. The values in { } are those of [5] and [29] respectively.

v level	$X^1\Sigma^+$ ($J = 0$)	$a^3\Pi$ ($J = 1$)
1	0.015 {0.013, 0.0125}	0.036 {0.034}
2	0.0075 {0.0068, 0.0065}	0.019 {0.018}
3	0.005 {0.0047, 0.0044}	0.013 {0.012}
4	0.0038 {0.0036, 0.0034}	0.011 {0.0095}
5	0.0033 {0.003, 0.0028}	0.009 {0.0078}

Table 2. Lifetimes, in seconds, of the rotational levels of the $X^1\Sigma^+$ state of CF^+.

J value	$X^1\Sigma^+$
1	179 537
2	18 701
3	5 171
4	2 104
5	1 053
6	600
7	374
8	248
9	173
10	126
20	15.3
30	4.5
40	1.89
50	0.97
60	0.56
70	0.35
80	0.24

The vibrational wavefunctions $\Psi_v(R)$ were evaluated for the CF^+ $X^1\Sigma^+$ potential energy from [3] and the CF^+ $a^3\Pi$ potential energy from [5]. The dipole moment functions $\mu(R)$ (in Debye) were taken from [5]. The molecular constants used in the evaluation of the transition energy $\Delta E_{vJ;v'J}$ were the spectroscopic values from [28] for CF^+ $X^1\Sigma^+$ and the MRCI calculated values from [5] for $a^3\Pi$. The results are presented in tables 1 and 2.

The results presented in table 2 are in good agreement with the values for vibrational state lifetimes calculated by Peterson *et al* [5] and Botschwina [29] though those authors did not present data for excited rotational states. Experimental determination of vibrational lifetimes for ground state CF^+ has been performed by Marx *et al* [30]. They found values of (23 ± 5) ms for $v \geqslant 1$ and (13.5 ± 3) ms for $v \geqslant 2$ but explained these larger values as being due to the repopulation of these levels by cascade from higher vibrational states ($v \geqslant 3$). By taking this into account, they were able to estimate apparent lifetimes of 18.9 ms and 10.5 ms, respectively, for $v \geqslant 1$ and $v \geqslant 2$ that are closer to the calculated values, shown in table 1.

It can be seen from tables 1 and 2 that the vibrationally excited levels should all radiate down to the $v = 0$ level during the storage of the ions in the ring prior to the recombination measurement. The $a^3\Pi$ state is also expected to have decayed as discussed in section 3. Rotationally excited levels of the $v = 0$ state, however, have very long lifetimes and if present upon injection into the ring, should stay excited during the measurement, thus explaining the high measured rotational temperature noted above.
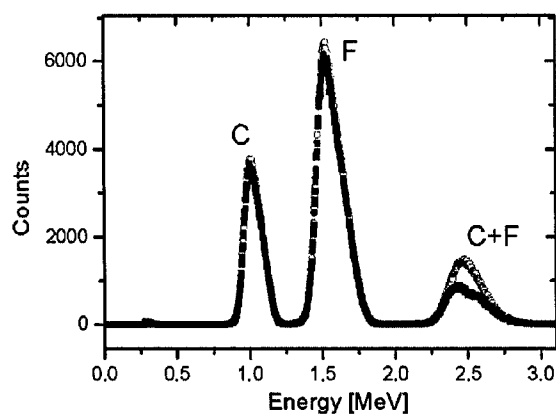
Figure 3. Pulse height spectrum of detector signals with electrons on (red open circles) and off (black dots).
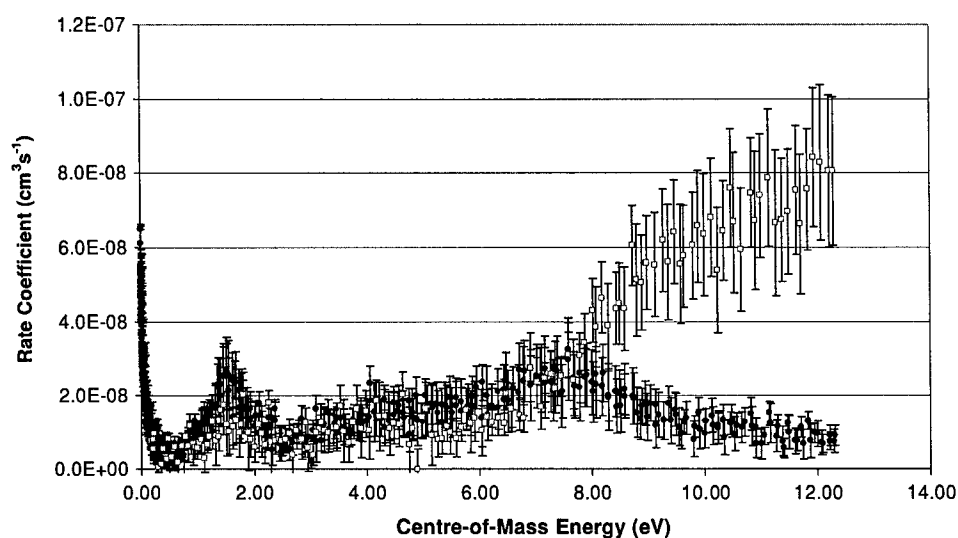

Figure 4. Measured $\langle \sigma v \rangle$ rate coefficients for electron–CF^+ collisions. Solid circles: signals from the C + F window. Open squares: signals from the F window.

5. Results and discussion

A typical pulse height spectrum accumulated during the experiment at ASTRID with the electron beam on and off and $E_{cm} = 0$ is shown in figure 3.

The three peaks in this spectrum correspond to C, F and C + F signals, the latter appearing at the full ion beam energy as the C and F atoms arrive simultaneously at the detector. The raw data for the measured $\langle \sigma v \rangle$ rate coefficient for electron–CF^+ collisions are shown in figure 4. The absolute values were only measured at CRYRING and the main error is due to the determination of the ion current. The absolute error is estimated to be ±20% and statistical errors due to counting statistics are shown for both the excitation and recombination channels.

The higher energy points (above 0.6 eV) were measured exclusively at ASTRID by using longer integration times.

These data were obtained from signals measured in the C + F window from the dissociative recombination reaction,
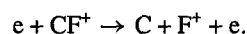
$$e + CF^+ \rightarrow C + F$$
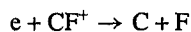
and from the F window due to the excitation reaction,

$$e + CF^+ \rightarrow C^+ + F + e.$$
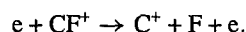
The energy threshold for the excitation reaction is 6.73 eV and 2.6 eV from the $v = 0$ levels of the ground $X^1\Sigma^+$ and metastable $a^3\Pi$ states respectively.

In the energy range examined, no positive signals were found in the C window corresponding to the reaction

$$e + CF^+ \rightarrow C + F^+ + e.$$

The threshold for dissociation to this channel from the CF^+ ground vibrational state lies at 12.89 eV and 8.78 eV from the metastable state. The highest centre-of-mass energy measured in this experiment was 12.3 eV for practical reasons and so one would not expect to have seen F atoms originating from the ground state. The fact that none at all were seen indicates that there is no contribution from the $a^3\Pi$ state that, as discussed in section 3, would have decayed before our measurements were taken.

It is seen that there is a low-energy peak in the recombination rate coefficient followed by a rather sharp distinct peak centred at about 1.5 eV and a broad diffuse peak centred at 7.5 eV. In the $C^+ + F$ excitation channel, there is a sharp onset of a rising rate at about 7 eV. In order to highlight the position of resonances and other features in these curves, we have plotted these data in the form of the Rate $\times E_{cm}$ versus E_{cm} and this is shown in figure 5(a) for the recombination signals and in figure 5(b) for the dissociative excitation channel.

The peak at 1.5 eV in the recombination rate is clearly seen followed by a steady rise up to 7.5 eV with a subsequent fall-off. There is no clear structure seen in the dissociative excitation channel below about 7 eV where an onset is observed with a fairly steady rise in the dissociative excitation cross section.

In order to interpret these observations, we reproduce in figure 6 the excited state potential energy curves for CF^+, calculated by Petsalakis and Theodorakopoulos [4]. From the spectroscopic constants calculated by these authors, which have been corroborated by photoelectron spectroscopic measurements of Dyke *et al* [31], the zero point energy of the ground $X^1\Sigma^+$ state is 0.11 eV and that of the $a^3\Pi$ state is 0.1 eV.

The first excited state ($a^3\Pi$) lies at 4.83 eV above the $v = 0$ level of the CF^+ ground state. This means that the 1.5 eV peak in the recombination rate must arise due to electron capture into neutral Rydberg states lying below the $a^3\Pi$ excited state of the CF^+ ion but above the ion ground state. Such processes have been seen for other molecular ions [32–34] and have been studied theoretically by Orel and co-workers [35, 36]. The peak centred at 7.58 eV must arise from capture into Rydberg states with the $1^1\Pi$ ion state as their limit.

Since the dissociation limit of CF^+ lies 6.73 eV above the $v = 0$ level, the $a^3\Pi$ does not contribute to the dissociative excitation process. The calculated vertical excitation energy of the $1^1\Pi$ state is 8.35 eV above the $v = 0$ level of the ground state and this corresponds quite well with the observed onset of the dissociative excitation cross section. The availability of higher lying states would make a further examination of this process interesting as it will be an important destruction mechanism under discharge conditions.

Recombination cross sections are plotted on a logarithmic scale in figure 7 in order to highlight the low-energy part of the spectrum. The cross section was obtained by dividing the
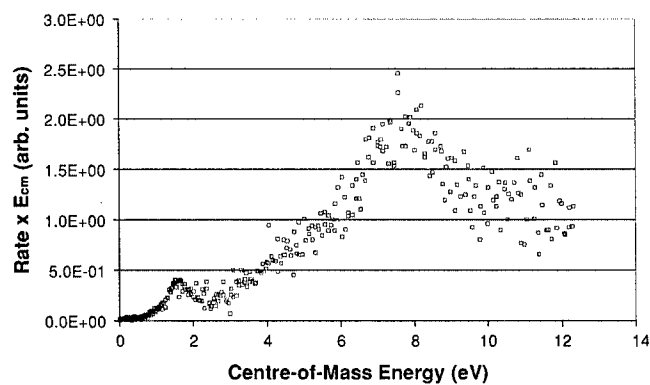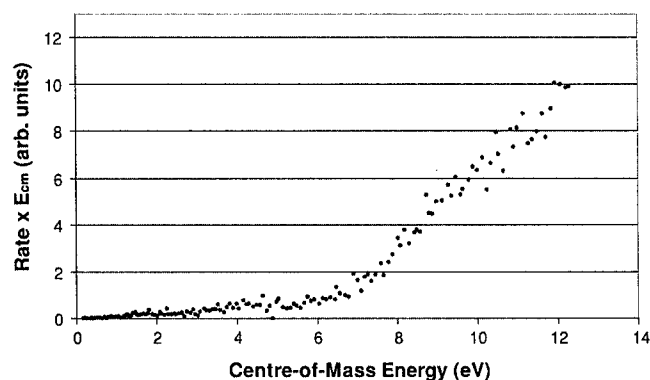
Figure 5. (a) $E_{cm} \times$ Rate plotted as a function of E_{cm} for the recombination channel. (b) $E_{cm} \times$ Rate plotted as a function of E_{cm} for the dissociative excitation channel.
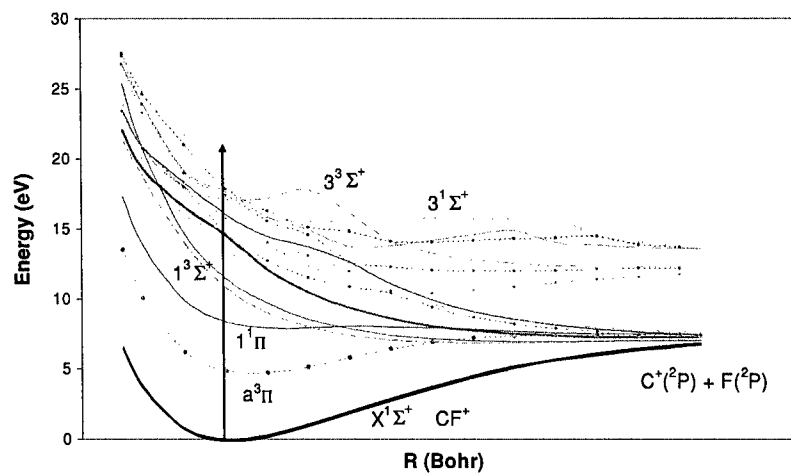

Figure 6. Potential energy curves for the ground and excited Σ and Π states of CF^+ [4]. Thick full curves: $^1\Sigma$ states; fine full curves: $^1\Pi$ states; dashed curves: $^3\Sigma$ states; dotted curves: $^3\Pi$ states.
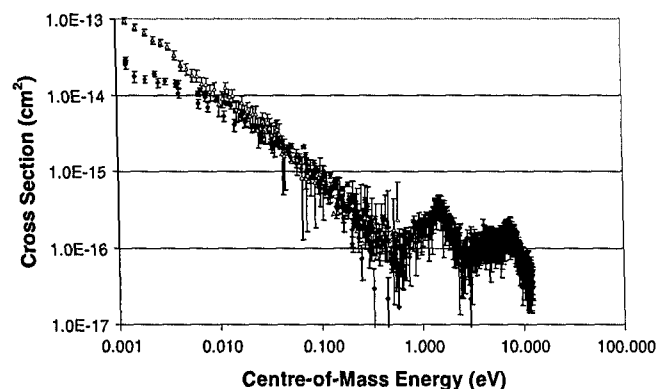
Figure 7. Measured cross sections for the recombination of CF^+. Solid diamonds: ASTRID data; open triangles: CRYRING data.

experimentally measured rate by the velocity. Data taken both at ASTRID and CRYRING are included. Both sets of data agreed very well with regard to the slope of the cross section and as mentioned above, the CRYRING data were used to normalize those taken at ASTRID. Since the energy resolution of the electron beam is better at CRYRING than at ASTRID it was possible to extend the measurements to lower energies by combining the results. Thus the divergence between the two data sets below 0.01 eV reflects the different energy resolutions at the two machines. The higher energy points (above 0.6 eV) were measured exclusively at ASTRID.

It can be seen from this figure that the cross sections at low energies are not very large even though it is seen in figure 1 that there should be several diabatic state curve crossings between the ion ground state and neutral states which would lead to a direct recombination process. This rather surprising observation should be an impetus for future theoretical studies. The data have been used to derive a thermal rate coefficient and this is found to have a value of $5.2 \pm 1.0 \times 10^{-8}$ $(T_e/300)^{-0.8}$ cm^3 s^{-1}, rather small for a diatomic ion where values of several times 10^{-7} cm^3 s^{-1} are more typical [37].

In summary, this study of the recombination and dissociative excitation processes for CF^+ has revealed some very interesting features that provide an impetus for further theoretical study. It has also served to increase, at least to a small extent, our knowledge of electron impact dissociation processes that drive the chemistry of technically important fluorocarbon plasmas, a subject that is still poorly understood due precisely to a lack of this kind of information.

Acknowledgments

Appendix

The Einstein coefficient for absorption is the probability for a dipole transition of frequency $\nu = \omega/c$. In SI units it is expressed as

$$A = \frac{q^2\omega^3}{3\pi\varepsilon_0 c^3 \hbar}|\vec{r}_{\mathrm{fi}}|^2$$

where $M = q\vec{r}_{\mathrm{fi}} = \langle\Psi_{\mathrm{f}}|q\vec{r}|\Psi_{\mathrm{i}}\rangle$ is the dipole matrix element between the initial and final states. For $q = e =$ electron charge in SI units, the previous expression can be found in the literature as

$$A = \text{factor} \times H \times \Delta E_{\mathrm{fi}}^3 \times M^2$$

with various numerical factors, depending on the units used for the transition energy $\Delta E_{\mathrm{fi}} = 2\pi\nu$ (m^{-1} in SI units) and for the dipole matrix element M (C m in SI). Expressing ΔE_{f} in m^{-1} in order to stay in SI units, three situations are frequently encountered as in [5, 27, 38]:

(i) If M is expressed in au $= 8.478 \times 10^{-30}$ C m (as in [5]), then the numerical factor is

$$\text{factor} = 2.023 \times 10^{-6}\frac{\mathrm{m}}{\mathrm{s}\,\mathrm{C}^2}.$$

(ii) If M is expressed in $e\mathrm{\AA} = 1.6 \times 10^{-29}$ C m (as in [27]), the numerical factor is

$$\text{factor} = 7.18 \times 10^{-6}\frac{\mathrm{m}}{\mathrm{s}\,\mathrm{C}^2}.$$

(iii) If M is expressed in Debye $= 3.338 \times 10^{-30}$ C m (as in [38]), the numerical factor is

$$\text{factor} = 3.12 \times 10^{-7}\frac{\mathrm{m}}{\mathrm{s}\,\mathrm{C}^2}.$$

The Einstein coefficient dimension is s^{-1}.

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