

# A study of the gas phase reactions of various cations with two derivatives of SF<sub>6</sub>; SF<sub>5</sub>CF<sub>3</sub> and SF<sub>5</sub>Cl

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A selected ion flow tube apparatus was used to investigate the positive ion chemistry of two derivatives of SF<sub>6</sub>; SF<sub>5</sub>CF<sub>3</sub> and SF<sub>5</sub>Cl. This represents the first investigation of the positive ion chemistry of SF<sub>5</sub>Cl, and much of the data on SF<sub>5</sub>CF<sub>3</sub> is being presented here for the first time. Rate coefficients and ion product branching ratios have been determined at room temperature (300 K) for reactions with the following twenty-two cations; Ne<sup>+</sup>, F<sup>+</sup>, Ar<sup>+</sup>, N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, CO<sup>+</sup>, CO<sub>2</sub><sup>+</sup>, O<sup>+</sup>, N<sub>2</sub>O<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, SF<sub>4</sub><sup>+</sup>, CF<sub>2</sub><sup>+</sup>, SF<sup>+</sup>, SF<sub>2</sub><sup>+</sup>, NO<sub>2</sub><sup>+</sup>, SF<sub>5</sub><sup>+</sup>, NO<sup>+</sup>, CF<sup>+</sup>, CF<sub>3</sub><sup>+</sup>, SF<sub>3</sub><sup>+</sup>, and H<sub>3</sub>O<sup>+</sup> (listed in order of decreasing recombination energy). Comparisons are made in the text for the reactions of these ions with SF<sub>6</sub>. SF<sub>2</sub><sup>+</sup>, NO<sub>2</sub><sup>+</sup>, NO<sup>+</sup>, SF<sub>3</sub><sup>+</sup>, and H<sub>3</sub>O<sup>+</sup> are found to be unreactive with both of the derivatives. The majority of the other reactions proceed with rate coefficients which are close to the capture value. The exceptions are the reactions of O<sub>2</sub><sup>+</sup>, SF<sup>+</sup>, SF<sub>5</sub><sup>+</sup>, and CF<sub>3</sub><sup>+</sup> with SF<sub>5</sub>CF<sub>3</sub>, and SF<sub>4</sub><sup>+</sup> and SF<sub>5</sub><sup>+</sup> with SF<sub>5</sub>Cl, all of which have rate coefficients significantly less than the capture mechanism value. Several distinct processes are observed among the large number of reactions studied, including dissociative charge transfer and various abstraction channels. Non-dissociative charge transfer is not observed, implying that any parent ions formed dissociate rapidly to the fragment ions and associated neutrals.

## 1. Introduction

There have been a number of investigations dealing with the positive ion chemistry of the important molecule sulfur hexafluoride, SF<sub>6</sub>.<sup>1–8</sup> These have been mostly associated with studies of the fundamental ion-molecule chemistry. Recent interest in this chemistry has come from the use of SF<sub>6</sub> in reactive plasmas for the etching of insulating and semiconductor layers.<sup>7</sup> Studies of the reactions of ions with SF<sub>6</sub> and related molecules enhance our understanding of the complex ion chemistry and kinetics involved in SF<sub>6</sub> containing plasmas. For example, the data obtained could be used to help model plasmas in order to ascertain which physical and chemical parameters will need to be varied in order to optimise the plasma environment for a particular application. In this paper we present a study of the reactions of a series of positive ions with two derivatives of SF<sub>6</sub>; trifluoromethyl sulfur pentafluoride, SF<sub>5</sub>CF<sub>3</sub>, and sulfur chloropentafluoride, SF<sub>5</sub>Cl, and compare them with the corresponding reactions for SF<sub>6</sub>.

Whilst the major stimulus for this investigation comes from its application to plasma ion chemistry, the recent detection of SF<sub>5</sub>CF<sub>3</sub> in the stratosphere provides additional motivation to this study.<sup>9</sup> As found for SF<sub>6</sub>, SF<sub>5</sub>CF<sub>3</sub> is not broken down by UV photodissociation in the stratosphere.<sup>10</sup> This leads naturally to the question as to whether there are any other atmospheric loss mechanisms. A recent electron attachment study shows that the molecule will be destroyed in the regions of the ionosphere where free electrons exist.<sup>11</sup> This provides an upper limit to the atmospheric lifetime of SF<sub>5</sub>CF<sub>3</sub> of ca. 1000 years. Other competitive routes in the ionosphere leading to the possible destruction of SF<sub>5</sub>CF<sub>3</sub> are reactions with ions. These may play a major role in the atmospheric lifetime of SF<sub>5</sub>CF<sub>3</sub> and hence have an impact on its global warming potential, which is currently estimated to be 18 000 times that of CO<sub>2</sub>.<sup>9</sup> A preliminary communication by us reported the first

gas-phase study of the reactions of SF<sub>5</sub>CF<sub>3</sub> with several positive ions of atmospheric interest.<sup>12</sup> A more detailed investigation of the reactions of a larger number of positive ions with this molecule is presented here. This includes cations of importance to industrial plasmas, e.g. F<sup>+</sup>, Ar<sup>+</sup>, SF<sub>5</sub><sup>+</sup>, CF<sup>+</sup>, CF<sub>3</sub><sup>+</sup>, and SF<sub>3</sub><sup>+</sup>. In addition, this paper presents the first reported ion-molecule chemistry of SF<sub>5</sub>Cl.

Rate coefficients and product ion branching ratios for thermal (300 K) reactions of SF<sub>5</sub>CF<sub>3</sub> and SF<sub>5</sub>Cl with the following cations of fundamental, atmospheric and/or plasma processing interest are reported: Ne<sup>+</sup>, F<sup>+</sup>, Ar<sup>+</sup>, N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, CO<sup>+</sup>, CO<sub>2</sub><sup>+</sup>, O<sup>+</sup>, N<sub>2</sub>O<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, SF<sub>4</sub><sup>+</sup>, CF<sub>2</sub><sup>+</sup>, SF<sup>+</sup>, SF<sub>2</sub><sup>+</sup>, NO<sub>2</sub><sup>+</sup>, SF<sub>5</sub><sup>+</sup>, NO<sup>+</sup>, CF<sup>+</sup>, CF<sub>3</sub><sup>+</sup>, SF<sub>3</sub><sup>+</sup>, and H<sub>3</sub>O<sup>+</sup>. These ions cover a large range of recombination energies, from 21.56 eV (Ne<sup>+</sup> + e<sup>−</sup> → Ne) to 6.27 eV (H<sub>3</sub>O<sup>+</sup> + e<sup>−</sup> → H<sub>2</sub>O + H). (1 eV = 96.4845 kJ mol<sup>−1</sup>.) Owing to this large range of available energies, several distinct reaction processes are observed amongst the large number of reactions studied, including dissociative charge transfer and various abstraction processes. For completeness, and ease of comparison, the results of the reactions of the above ions with SF<sub>6</sub> collected from various published papers are also presented here. Where results for SF<sub>6</sub> are unavailable in the literature, additional experiments have been performed as part of this investigation, the data from which are presented here.

## 2. Experimental

The selected ion flow tube (SIFT) apparatus used to obtain the reaction rate coefficients and product ion branching ratios has been described in detail elsewhere,<sup>13,14</sup> so only a brief overview of the salient points of the experimental technique is included here. The reagent ions were generated in an electron impact high-pressure ion source containing an appropriate gas

(Ne for  $\text{Ne}^+$ ,  $\text{CF}_4$  for  $\text{F}^+$  and  $\text{CF}_m^+$  ( $m = 1-3$ ), Ar for  $\text{Ar}^+$ ,  $\text{N}_2$  for  $\text{N}_2^+$  and  $\text{N}^+$ , CO for  $\text{CO}^+$ ,  $\text{CO}_2$  for  $\text{CO}_2^+$ ,  $\text{N}_2\text{O}$  for  $\text{O}^+$ ,  $\text{NO}^+$  and  $\text{N}_2\text{O}^+$ ,  $\text{H}_2\text{O}$  for  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$ ,  $\text{O}_2$  for  $\text{O}_2^+$ ,  $\text{SF}_6$  for  $\text{SF}_n^+$  ( $n = 1-5$ ), and  $\text{NO}_2$  for  $\text{NO}_2^+$ ). The reagent ions were mass selected using a quadrupole mass filter, before being injected into a 300 K helium carrier gas at a pressure of *ca.* 0.5 Torr. The helium gas (high-purity grade (99.997%)) was passed through a liquid nitrogen cooled zeolite trap before use. The reagent ions were transported along the flow tube and detected by a downstream quadrupole mass spectrometer detection system. Neutral reactant gas was added in controlled amounts to the ion swarm/carrier gas.

The loss of the reagent ions and the appearance of product ions were monitored by the detection system. Relaxed resolution on the quadrupole mass spectrometer, in order to minimize mass discrimination effects, was used in the determination of the branching ratios. The reaction rate coefficients and ion product distributions were then determined in the usual way.<sup>13-15</sup> Reaction rate coefficients, which were extracted from linear least-squares fits of the plot of the logarithm of the reagent ion signal *versus* reactant neutral concentration, are considered to be accurate to  $\pm 20\%$ . The percentage product ion branching ratios, determined from the product ion counts as a function of reactant neutral concentration and extrapolated to zero flow conditions to allow for secondary reactions, are only used to provide a qualitative indication of the relative importance of different channels, and therefore accurate values are not important in our discussions. However, a statistical analysis on the branching ratios indicates a fractional accuracy of better than 20% for the reaction channels with branching ratios greater than 10%. For ion channels with branching ratios less than this value, the accuracy is reduced. For the ion channels with branching ratios of only 1%, the uncertainty is as high as  $\pm 100\%$ .

The high pressure of the gases used in the ionisation source, *ca.* several Torr, should help to quench electronically and/or vibrationally excited states of molecular ions prior to their injection into the flow tube. However, quenching of vibrational states is not assured, as confirmed by studies on the  $\text{O}_2^+$  reagent ion. Whilst the majority of the  $\text{O}_2^+$  ions were found to be in the  $v = 0$  level, approximately 30% were found to be in the  $v = 1$  and 2 vibrational levels. This was established from observed reactions with Xe and  $\text{SO}_2$ . The lack of a reaction of the reagent ion  $\text{O}_2^+$  with  $\text{H}_2\text{O}$  showed that the  $v \geq 3$  vibrational levels of  $\text{O}_2^+$  were not populated. Similarly, for the  $\text{N}_2^+$  reagent ions, reaction with Ar indicated that approximately 40% of the  $\text{N}_2^+$  ions were in the  $v = 1$  vibrational level. It is possible that other reagent molecular ions had internal energies above the thermal value. However, no curvature was observed in any of the pseudo-first-order kinetic plots, indicating that rate coefficients are the same for reactions involving the ground and any vibrationally excited states. This does not rule out reagent ion vibrational excitation influencing the ion product distributions for those reactions which produce more than one ion product.

Atomic ions are expected to be in their ground electronic states prior to reaction with a neutral molecule. Thus  $\text{Ar}^+$  and  $\text{Ne}^+$  should emerge from the high-pressure ion source in their lowest energy,  $^2\text{P}_{3/2}$  states. Even if this were not the case, the energy separation between the  $^2\text{P}_{3/2}$  and  $^2\text{P}_{1/2}$  states is only 0.18 eV for  $\text{Ar}^+$  and 0.10 eV for  $\text{Ne}^+$ , and therefore differences in reactivities between the two spin-orbit states are not expected. No evidence was found for differences in the reaction rate coefficients of the  $^2\text{P}_{3/2}$  and  $^2\text{P}_{1/2}$  states. Whether differences in branching ratios result from reactions involving these two spin-orbit states is more difficult to assess, but given the small differences in energy, none are expected. The ground state of  $\text{F}^+$  is a closely-spaced triplet with recombination energies of 17.42 eV ( $^3\text{P}_2$ ), 17.47 eV ( $^3\text{P}_1$ ) and 17.48 eV ( $^3\text{P}_0$ ). Thus, for this ion, there will be significant population in all three

states. As for  $\text{Ar}^+$  and  $\text{Ne}^+$ , no differences in the reactivity of the  $\text{F}^+$  ion in its various spin-orbit states are to be expected. For the other two atomic ions used in this investigation, electronically excited states of  $\text{N}^+$  and  $\text{O}^+$  have previously been shown not to be present.<sup>16</sup>

Water contamination in the flow tube and He buffer gas flow resulted in electron transfer from  $\text{H}_2\text{O}$  to those injected ions whose recombination energies are greater than the ionisation potential of  $\text{H}_2\text{O}$ , 12.62 eV. This resulted in an  $\text{H}_2\text{O}^+$  signal, which was usually less than 5% of the parent ion signal. Product ion branching ratios have been corrected for the contribution to the signals resulting from the reaction with  $\text{H}_2\text{O}^+$ . Some of the  $\text{H}_2\text{O}^+$  was converted to  $\text{H}_3\text{O}^+$  in the flow tube ( $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$ ). This caused no problem in the determination of the product ion branching ratios, because  $\text{H}_3\text{O}^+$  is unreactive with  $\text{SF}_5\text{CF}_3$ ,  $\text{SF}_5\text{Cl}$ , and  $\text{SF}_6$ . Experiments with  $\text{H}_2\text{O}^+$  as the reagent ion presented a separate problem, for it was found that  $\text{OH}^+$  and  $\text{H}_3\text{O}^+$  ions were being injected into the flow tube together with  $\text{H}_2\text{O}^+$ . Again, because the  $\text{H}_3\text{O}^+$  ions are unreactive with both  $\text{SF}_5\text{CF}_3$  and  $\text{SF}_5\text{Cl}$ , their presence in the flow tube could be ignored. However, it was observed from the decrease in the  $\text{OH}^+$  signal as a function of neutral concentration that this ion reacts efficiently with  $\text{SF}_5\text{CF}_3$  and  $\text{SF}_5\text{Cl}$ . Reduction of the injection ion energy, which insured that the  $\text{OH}^+$  was not produced by collision-induced dissociation, did not remove the problem. Attempts to eliminate the  $\text{OH}^+$  signal by increasing the resolution of the injection mass spectrometer drastically reduced the  $\text{H}_2\text{O}^+$  signal. The best compromise between  $\text{OH}^+$  rejection and  $\text{H}_2\text{O}^+$  signal gave a reagent ion flux comprised of 5%  $\text{OH}^+$  and 95%  $\text{H}_2\text{O}^+$ . No allowances have been made for the (small) contributions due to the  $\text{OH}^+$  reaction to the branching ratios for the reaction of  $\text{H}_2\text{O}^+$  with either  $\text{SF}_5\text{CF}_3$  or  $\text{SF}_5\text{Cl}$ . Reaction rate coefficients and product ions for the reaction with  $\text{OH}^+$  were not obtained.  $\text{OH}^+$  was also produced in the flow tube when  $\text{Ne}^+$  was used as the reagent ion. Again, the  $\text{OH}^+$  signal was small (approximately 5% of that of  $\text{Ne}^+$ ) and was ignored in the determination of product ion branching ratios.  $\text{Ne}^+$  also resulted in the formation of  $\text{HeNe}^+$  cations in the flow tube from termolecular association, which led to a  $\text{HeNe}^+$  signal of about 2%–3% of the  $\text{Ne}^+$  signal. Given the low percentage of this impurity ion in the flow tube, its contributions to the yields of the product ions for  $\text{Ne}^+$  were reasonably neglected.

The samples of the reactant neutrals,  $\text{SF}_5\text{CF}_3$  and  $\text{SF}_5\text{Cl}$ , were commercially purchased (Apollo Scientific Limited, Whaley Bridge, Derbyshire, UK) with stated purities of 99% and 97%, respectively. They were used in the experiments without further purification. The  $\text{SF}_6$  was purchased from Fluorochem Limited, Old Glossop, Derbyshire, UK with a stated purity of >99%. This sample was also used directly without additional purification.

### 3. Results and discussion

The experimental rate coefficients,  $k_{\text{exp}}$ , the observed product ions, and their branching ratios for the reactions of  $\text{SF}_5\text{CF}_3$ ,  $\text{SF}_5\text{Cl}$  and  $\text{SF}_6$  with 22 different reagent ions are given in Tables 1–3, respectively. The reagent ions are listed (top to bottom) in order of decreasing recombination energy (RE). Where no reaction was observed, this implies that the experimental rate coefficient,  $k_{\text{exp}} < 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The majority of the  $\text{SF}_6$  data presented in Table 3 has been collected from the literature,<sup>1-8</sup> and are given here to aid comparison. In the cases of the reactions with  $\text{SF}_6$  for which no published data exist, we have made the appropriate measurements to complete Table 3.

To assess the efficiency of the reactions, the experimental rate coefficients are compared in the tables with the predictions

**Table 1** The measured 300 K reaction rate coefficients (in units of  $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ), cation product ions, their branching ratios (percentages), suggested neutral products and 0 K enthalpies for the reactions of  $\text{Ne}^+$ ,  $\text{F}^+$ ,  $\text{Ar}^+$ ,  $\text{N}_2^+$ ,  $\text{N}^+$ ,  $\text{CO}^+$ ,  $\text{CO}_2^+$ ,  $\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{O}_2^+$ ,  $\text{SF}_4^+$ ,  $\text{CF}_2^+$ ,  $\text{SF}^+$ ,  $\text{SF}_2^+$ ,  $\text{NO}_2^+$ ,  $\text{SF}_5^+$ ,  $\text{NO}^+$ ,  $\text{CF}^+$ ,  $\text{CF}_3^+$ ,  $\text{SF}_3^+$  and  $\text{H}_3\text{O}^+$  with  $\text{SF}_5\text{CF}_3$  are presented. The recombination energies of the reagent cations are listed in eV in round brackets under the cations. The value in square brackets is the fluoride affinity of the reagent cation. The capture rate coefficients, calculated using parametrized fits to results from trajectory calculations,<sup>18</sup> are presented in square brackets under the experimental values. The measured rate coefficients are considered to be accurate to  $\pm 20\%$ . When dissociative charge transfer is exothermic, only this channel is represented in the table, with the neutrals assembled to give the lowest reaction enthalpy. The trace given for the  $\text{SF}_4^+$  product ion for a number of reactions and for  $\text{SF}_4\text{CF}_3^+$  from the reaction with  $\text{CF}_2^+$  represents a detectable signal with our apparatus, but whose branching ratio is less than 1%. 0 K enthalpies of formation for  $\text{CF}_m^+$ ,  $\text{CF}_m$ ,<sup>24</sup> and for  $\text{SF}_n$ ,  $\text{SF}_n^{+25}$  are taken from recent high level *ab initio* calculations.  $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3) = -1673 \text{ kJ mol}^{-1}$  (see text). Other 0 K enthalpy data are taken from the JANAF tabulations,<sup>27</sup> information available at the NIST website,<sup>51</sup> and additional sources of data as identified in the table footnotes. The major source of uncertainty in the values is  $\pm 40 \text{ kJ mol}^{-1}$  in  $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3)$

Reagent ion	Rate coefficient/ $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Product ion (%)	Proposed neutral products	$\Delta_f H_0^\circ/\text{kJ mol}^{-1}$
$\text{Ne}^+$ (21.56) [1753]	1.5 [1.8]	$\text{CF}_3^+$ (47) $\text{SF}_2^+$ (5) $\text{SF}_3^+$ (37) $\text{SF}_4^+$ (1) $\text{SF}_5^+$ (10)	$\text{SF}_5 + \text{Ne}$ $\text{CF}_4 + \text{F}_2 + \text{Ne}$ $\text{CF}_4 + \text{F} + \text{Ne}$ $\text{CF}_4 + \text{Ne}$ $\text{CF}_3 + \text{Ne}$	-836 -645 -898 -946 -786
$\text{F}^+$ (17.42) [1508]	1.6 [1.9]	$\text{CF}_3^+$ (73) $\text{SF}_3^+$ (24) $\text{SF}_4^+$ (trace) $\text{SF}_5^+$ (3)	$\text{SF}_5 + \text{F}$ $\text{CF}_4 + \text{F} + \text{F}$ $\text{CF}_4 + \text{F}$ $\text{CF}_3 + \text{F}$	-436 -498 -546 -386
$\text{Ar}^+$ (15.76) [1193]	1.4 [1.3]	$\text{CF}_3^+$ (65) $\text{SF}_3^+$ (30) $\text{SF}_5^+$ (4) $\text{SF}_4\text{CF}_3^+$ (1)	$\text{SF}_5 + \text{Ar}$ $\text{CF}_4 + \text{F} + \text{Ar}$ $\text{CF}_3 + \text{Ar}$ $\text{F} + \text{Ar}$	-276 -338 -226 $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+) + 230$
$\text{N}_2^+$ (15.58) [1175]	1.6 [1.6]	$\text{CF}_3^+$ (65) $\text{SF}_3^+$ (28) $\text{SF}_4^+$ (trace) $\text{SF}_5^+$ (5) $\text{SF}_4\text{CF}_3^+$ (2)	$\text{SF}_5 + \text{N}_2$ $\text{CF}_4 + \text{F} + \text{N}_2$ $\text{CF}_4 + \text{N}_2$ $\text{CF}_3 + \text{N}_2$ $\text{F} + \text{N}_2$	-259 -321 -368 -209 $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+) + 247$
$\text{N}^+$ (14.53) [1374]	2.2 [2.1]	$\text{CF}_3^+$ (80) $\text{SF}_3^+$ (17) $\text{SF}_4^+$ (trace) $\text{SF}_5^+$ (3)	$\text{SF}_5 + \text{N}$ $\text{CF}_4 + \text{F} + \text{N}$ $\text{CF}_4 + \text{N}$ $\text{CF}_3 + \text{N}$	-158 -220 -267 -108
$\text{CO}^+$ (14.01) [1173] <sup>a</sup>	1.6 [1.6]	$\text{CF}_3^+$ (75) $\text{SF}_3^+$ (22) $\text{SF}_4^+$ (trace) $\text{SF}_5^+$ (3)	$\text{SF}_5 + \text{CO}$ $\text{CF}_4 + \text{F} + \text{CO}$ $\text{CF}_4 + \text{CO}$ $\text{CF}_3 + \text{CO}$	-107 -169 -217 -57
$\text{CO}_2^+$ (13.78) [1049] <sup>b</sup>	1.2 [1.3]	$\text{CF}_3^+$ (76) $\text{SF}_3^+$ (14) $\text{SF}_4^+$ (8) $\text{SF}_5^+$ (2)	$\text{SF}_5 + \text{CO}_2$ $\text{CF}_4 + \text{F} + \text{CO}_2$ $\text{CF}_4 + \text{CO}_2$ $\text{CF}_3 + \text{CO}_2$	-85 -147 -194 -35
$\text{O}^+$ (13.62) [1202]	1.9 [2.0]	$\text{CF}_3^+$ (83) $\text{SF}_3^+$ (16) $\text{SF}_4^+$ (trace) $\text{SF}_5^+$ (1)	$\text{SF}_5 + \text{O}$ $\text{CF}_4 + \text{F} + \text{O}$ $\text{CF}_4 + \text{O}$ $\text{CF}_3 + \text{O}$	-69 -131 -179 -19
$\text{N}_2\text{O}^+$ (12.89) [971]	1.1 [1.3]	$\text{CF}_3^+$ (75) $\text{SF}_3^+$ (19) $\text{SF}_4^+$ (5) $\text{SF}_5^+$ (1)	$\text{SF}_5 + \text{N}_2\text{O}$ $\text{CF}_4 + \text{F} + \text{N}_2\text{O}$ $\text{CF}_4 + \text{N}_2\text{O}$ $\text{CF}_3\text{O} + \text{N}_2$	+1 -61 -109 -203 <sup>c</sup>
$\text{H}_2\text{O}^+$ (12.62) [962]	1.6 [1.9]	$\text{CF}_3^+$ (8) $\text{SF}_3^+$ (92)  $\text{SF}_4^+$ (trace)	$\text{CF}_2\text{O} + \text{N}_2 + \text{F}$ $\text{SF}_5 + \text{H}_2\text{O}$ $\text{CF}_4 + \text{F} + \text{H}_2\text{O}$ $\text{CF}_4 + \text{HF} + \text{OH}$ $\text{CF}_4 + \text{H}_2\text{O}$	+27 -35 -108 -83
$\text{O}_2^+$ (12.07) [887]	0.01 [1.5]	$\text{CF}_3^+$ (63)  $\text{SF}_3^+$ (31)  $\text{SF}_4^+$ (2) $\text{SF}_5^+$ (4)	$\text{SF}_5 + \text{O}_2$ $\text{SF}_5\text{O}_2$ $\text{CF}_4 + \text{F} + \text{O}_2$ $\text{CF}_4 + \text{FO}_2$ $\text{CF}_4 + \text{O}_2$ $\text{CF}_3 + \text{O}_2$	+80, +58, +36 <sup>e</sup> 29 <sup>f</sup> 18 -32 -29 130
$\text{SF}_4^+$ (11.92) [976]	0.17 [0.92]	$\text{SF}_3^+$ (100%)	$\text{CF}_3\text{O}_2$ $\text{CF}_4 + \text{SF}_5$	-33 <sup>g</sup> -121
$\text{CF}_2^+$ (11.43) [1122]	1.1 [1.2]	$\text{CF}_3^+$ (38)  $\text{SF}_3^+$ (60) $\text{SF}_5^+$ (2) $\text{SF}_4\text{CF}_3^+$ (trace)	$\text{SF}_4 + \text{CF}_3$ $\text{SF}_3 + \text{CF}_4$ $\text{CF}_3 + \text{CF}_4$ $\text{C}_2\text{F}_5$ $\text{CF}_3$	-52 -193 -267 -49 <sup>h</sup> $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+) + 301$

**Table 1** (continued)

Reagent ion	Rate coefficient/ $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Product ion (%)	Proposed neutral products	$\Delta_r H_0^\circ / \text{kJ mol}^{-1}$
SF <sup>+</sup> (10.25) [1034]	0.03 [1.2]	CF <sub>3</sub> <sup>+</sup> (44) SF <sub>3</sub> <sup>+</sup> (56)	SF <sub>2</sub> + SF <sub>4</sub> CF <sub>4</sub> + SF <sub>2</sub>	+ 36 −179
SF <sub>2</sub> <sup>+</sup> (10.17) [876]	no reaction			
NO <sub>2</sub> <sup>+</sup> (9.59) [607]	no reaction			
SF <sub>5</sub> <sup>+</sup> (9.55) [1040]	0.14 [0.88]	CF <sub>3</sub> <sup>+</sup> (13) SF <sub>3</sub> <sup>+</sup> (87)	SF <sub>4</sub> + SF <sub>6</sub> SF <sub>6</sub> + CF <sub>4</sub>	+ 30 −185
NO <sup>+</sup> (9.26) [797]	no reaction			
CF <sup>+</sup> (9.10) [1066]	1.2 [1.5]	CF <sub>3</sub> <sup>+</sup> (47) SF <sub>3</sub> <sup>+</sup> (51)	CF <sub>4</sub> + SF <sub>2</sub> CF <sub>2</sub> + SF <sub>4</sub> CF <sub>2</sub> + CF <sub>4</sub> C <sub>2</sub> F <sub>6</sub>	−261 + 4 −211 −431 <sup>i</sup>
CF <sub>3</sub> <sup>+</sup> (9.03) [1085]	0.48 [1.1]	SF <sub>5</sub> <sup>+</sup> (2) SF <sub>3</sub> <sup>+</sup> (98) SF <sub>5</sub> <sup>+</sup> (2)	C <sub>2</sub> F <sub>4</sub> CF <sub>4</sub> + CF <sub>4</sub> C <sub>2</sub> F <sub>6</sub>	−40 <sup>j</sup> −230 + 8 <sup>i</sup>
SF <sub>3</sub> <sup>+</sup> (8.26) [870]	no reaction			
H <sub>3</sub> O <sup>+</sup> (6.27) [843]	no reaction			

<sup>a</sup>  $\Delta_r H_0^\circ(\text{FCO}) = -185 \text{ kJ mol}^{-1}$  from Dixon and Feller.<sup>52</sup> <sup>b</sup>  $D_0(\text{F-CO}_2) = 48 \text{ kJ mol}^{-1}$  from Arnold *et al.*<sup>39</sup> <sup>c</sup>  $\Delta_r H_0^\circ(\text{CF}_3\text{O}) = -630 \text{ kJ mol}^{-1}$  from Louis *et al.*<sup>53</sup> <sup>d</sup>  $\Delta_r H_0^\circ(\text{CF}_2\text{O}) = -603 \text{ kJ mol}^{-1}$  from Louis *et al.*<sup>53</sup> <sup>e</sup> The values given are for the  $v = 0, 1$  and  $2$  vibrational levels of  $\text{O}_2^+$ , respectively. Energy levels calculated using  $\text{O}_2^+$  ground state vibrational spectroscopic constants from Huber and Herzberg.<sup>54</sup> <sup>f</sup>  $D_0(\text{SF}_5\text{-O}_2) = 51 \text{ kJ mol}^{-1}$  estimated from  $\Delta_r H_{295}^\circ(\text{SF}_5\text{O}_2 \rightarrow \text{SF}_5 + \text{O}_2) = 57.3 \text{ kJ mol}^{-1}$  obtained by Sehested *et al.*<sup>55</sup> <sup>g</sup>  $D_0(\text{CF}_3\text{-O}_2) = 163 \text{ kJ mol}^{-1}$  from Louis *et al.*<sup>53</sup> <sup>h</sup>  $\Delta_r H_0^\circ(\text{CF}_3\text{CF}_2) = -896 \text{ kJ mol}^{-1}$  from Bauschlicher and Ricca.<sup>47</sup> <sup>i</sup>  $\Delta_r H_0^\circ(\text{CF}_3\text{CF}_3) = -1341 \text{ kJ mol}^{-1}$  from Bauschlicher and Ricca.<sup>47</sup> <sup>j</sup>  $\Delta_r H_0^\circ(\text{CF}_2\text{CF}_2) = -673 \text{ kJ mol}^{-1}$  from Bauschlicher and Ricca.<sup>47</sup>

of capture theory,  $k_c$ . Essential pieces of information for making capture theory calculations of  $k_c$  are the polarisability and the dipole moment of the neutral reactant molecule. Neither of these quantities are available in the literature for SF<sub>5</sub>CF<sub>3</sub> and SF<sub>5</sub>Cl. The polarisabilities of SF<sub>5</sub>CF<sub>3</sub> and SF<sub>5</sub>Cl have been estimated to be  $8.44 \times 10^{-30} \text{ m}^3$  and  $8.38 \times 10^{-30} \text{ m}^3$ , respectively, using Miller and Savchik's empirical approach.<sup>17</sup> At the Hartree-Fock level, the dipole moments for SF<sub>5</sub>CF<sub>3</sub> and SF<sub>5</sub>Cl have been calculated to be 0.95 and 0.93 D, respectively. Given these values the capture rate coefficients can be estimated using the results of parameterised fits to trajectory calculations,<sup>18</sup> and these  $k_c$  values appear in square brackets in Tables 1 and 2. A comparison of the experimental rate coefficients with the capture values provides a good indication of whether a reaction is efficient, with most captures leading to reaction, or inefficient. The capture rate coefficients are readily determined for the centrosymmetric molecule SF<sub>6</sub> using the Langevin equation,<sup>19</sup> and a value for the polarisability of SF<sub>6</sub> ( $= 6.54 \times 10^{-30} \text{ m}^3$ <sup>20</sup>). These  $k_c$  values are presented in Table 3.

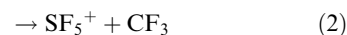
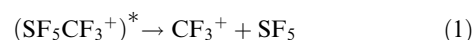
The determination of reaction pathways requires knowledge of the ion and neutral products. In our experiments, only the masses and relative yields of the ion products are determined, so the neutral products can only be inferred from mass balance and thermochemical arguments. The thermochemical analysis is restricted to considerations of enthalpy at 0 K (*i.e.*  $\Delta_r H_0^\circ < 0$  for an observable reaction), and we have ignored any entropic effects. In the tables we have generally listed the neutrals which give the most exothermic pathway to a particular

observed ion product, so that the maximum energy is available for partitioning between the internal and translational degrees of freedom. In many cases there is sufficient energy to break chemical bonds in the neutral products.

### 3.1 SF<sub>5</sub>CF<sub>3</sub> reactions

An investigation of the reactions of a number of positive ions of atmospheric interest (N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, CO<sup>+</sup>, CO<sub>2</sub><sup>+</sup>, O<sup>+</sup>, N<sub>2</sub>O<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, NO<sub>2</sub><sup>+</sup>, NO<sup>+</sup>, and H<sub>3</sub>O<sup>+</sup>) with SF<sub>5</sub>CF<sub>3</sub> has recently been reported by us.<sup>12</sup> A more extensive study, which includes many additional ions, *i.e.* Ne<sup>+</sup>, F<sup>+</sup>, Ar<sup>+</sup>, SF<sub>4</sub><sup>+</sup>, CF<sub>2</sub><sup>+</sup>, SF<sup>+</sup>, SF<sub>2</sub><sup>+</sup>, SF<sub>5</sub><sup>+</sup>, CF<sup>+</sup>, CF<sub>3</sub><sup>+</sup>, and SF<sub>3</sub><sup>+</sup>, is presented here. The experimental reaction rate coefficients, the observed product ions, and their percentage branching ratios are given in Table 1.

Dissociative charge transfer is almost certainly the dominant reaction mechanism for reagent ions whose recombination energies are greater than about 12.5 eV. The overall process can be viewed as a two step mechanism, transfer of an electron from the reactant neutral to the reagent ion (often described as occurring at long range), followed by fragmentation of the unstable intermediate ion, here (SF<sub>5</sub>CF<sub>3</sub>)<sup>+</sup>, with the newly formed neutral acting as a spectator. Simple dissociations such as:



**Table 2** The measured 300 K reaction rate coefficients (in units of  $10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), cation product ions, their branching ratios (percentages), suggested neutral products and 0 K enthalpies for the reactions of Ne<sup>+</sup>, F<sup>+</sup>, Ar<sup>+</sup>, N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, CO<sup>+</sup>, CO<sub>2</sub><sup>+</sup>, O<sup>+</sup>, N<sub>2</sub>O<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, SF<sub>4</sub><sup>+</sup>, CF<sub>2</sub><sup>+</sup>, SF<sup>+</sup>, SF<sub>2</sub><sup>+</sup>, NO<sub>2</sub><sup>+</sup>, SF<sub>5</sub><sup>+</sup>, NO<sup>+</sup>, CF<sup>+</sup>, CF<sub>3</sub><sup>+</sup>, SF<sub>3</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup> with SF<sub>5</sub>Cl are presented. The recombination energies of the reagent cations are listed in eV in brackets under the cations. The value in square brackets is the fluoride affinity of the reagent cation. The capture rate coefficients, calculated using parametrized fits to results from trajectory calculations,<sup>18</sup> are presented in square brackets under the experimental values. The measured rate coefficients are considered to be accurate to  $\pm 20\%$ . It is assumed that ClF<sub>2</sub> and ClF<sub>3</sub> are not formed in dissociative charge-transfer reactions. When dissociative charge transfer is exothermic, only this channel is represented in the table, with the neutrals assembled to give the lowest reaction enthalpy. The trace given for the SF<sub>3</sub><sup>+</sup> and SF<sub>2</sub>Cl<sup>+</sup> product ions resulting from the reaction with CO<sub>2</sub><sup>+</sup> represents a detectable signal with our apparatus, but whose branching ratio is less than 1%. 0 K enthalpies of formation for CF<sub>m</sub><sup>+</sup>, CF<sub>m</sub>,<sup>24</sup> and for SF<sub>n</sub>, SF<sub>n</sub><sup>+</sup><sup>25</sup> are taken from recent high level *ab initio* calculations.  $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3) = -985$  kJ mol<sup>-1</sup> (see text). Other 0 K enthalpy data are taken from the JANAF tabulations,<sup>27</sup> information available at the NIST website,<sup>51</sup> and additional sources of data as identified in the table footnotes

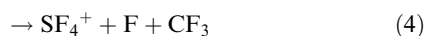
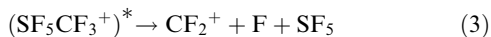
Reagent ion	Rate coefficient/ $10^{-9}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Product ion (%)	Proposed neutral products	$\Delta_f H_0^\circ/\text{kJ mol}^{-1}$ <sup>a</sup>
Ne <sup>+</sup> (21.56) [1753]	1.7 [1.8]	Cl <sup>+</sup> (4) SF <sub>2</sub> <sup>+</sup> (trace) SF <sub>3</sub> <sup>+</sup> (86) SF <sub>4</sub> <sup>+</sup> (1) SF <sub>5</sub> <sup>+</sup> (5) SF <sub>4</sub> Cl <sup>+</sup> (4)	SF <sub>5</sub> + Ne ClF + F <sub>2</sub> + Ne ClF + F + Ne ClF + Ne Cl + Ne F + Ne	-562 -457 -709 -757 -892 -868 <sup>a</sup>
F <sup>+</sup> (17.42) [1508]	1.9 [1.9]	SF <sub>3</sub> <sup>+</sup> (19) SF <sub>4</sub> <sup>+</sup> (30) SF <sub>5</sub> <sup>+</sup> (19) SF <sub>4</sub> Cl <sup>+</sup> (32)	ClF + F + F ClF + F Cl + F F + F	-309 -357 -492 -623 <sup>a</sup>
Ar <sup>+</sup> (15.76) [1193]	1.3 [1.4]	SF <sub>5</sub> <sup>+</sup> (47) SF <sub>4</sub> Cl <sup>+</sup> (53)	Cl + Ar F + Ar	-332 -308 <sup>a</sup>
N <sub>2</sub> <sup>+</sup> (15.58) [1175]	1.6 [1.6]	SF <sub>5</sub> <sup>+</sup> (52) SF <sub>4</sub> Cl <sup>+</sup> (48)	Cl + N <sub>2</sub> F + N <sub>2</sub>	-315 -291 <sup>a</sup>
N <sup>+</sup> (14.53) [1374]	1.9 [2.1]	SF <sub>3</sub> <sup>+</sup> (3) SF <sub>5</sub> <sup>+</sup> (77) SF <sub>4</sub> Cl <sup>+</sup> (20)	ClF + F + N Cl + N F + N	-31 -214 -190 <sup>a</sup>
CO <sup>+</sup> (14.01) [1173]	1.6 [1.6]	SF <sub>5</sub> <sup>+</sup> (50) SF <sub>4</sub> Cl <sup>+</sup> (50)	Cl + CO F + CO	-163 -140 <sup>a</sup>
CO <sub>2</sub> <sup>+</sup> (13.78) [1049] <sup>b</sup>	1.2 [1.3]	SFCl <sup>+</sup> (5) SF <sub>3</sub> <sup>+</sup> (trace) SF <sub>2</sub> Cl <sup>+</sup> (trace)  SF <sub>5</sub> <sup>+</sup> (93) SF <sub>4</sub> Cl <sup>+</sup> (2) SF <sub>5</sub> <sup>+</sup> (84) SF <sub>4</sub> Cl <sup>+</sup> (16)	CF <sub>4</sub> + O <sub>2</sub> ClF <sub>2</sub> + CO <sub>2</sub> CF <sub>2</sub> O + FO CF <sub>3</sub> O <sub>2</sub> Cl + CO <sub>2</sub> F + CO <sub>2</sub> Cl + O F + O	$\Delta_f H_0^\circ(\text{SFCl}^+)^c - 878$ -90 <sup>d</sup> $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+)^e - 446^f$ $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+)^e - 591^g$ -141 -117 <sup>a</sup> -125 -102 <sup>a</sup>
O <sup>+</sup> (13.62) [1202]	2.0 [2.0]	SF <sub>5</sub> <sup>+</sup> (98) SF <sub>4</sub> Cl <sup>+</sup> (2)	Cl + N <sub>2</sub> O F + N <sub>2</sub> O	-55 -31
N <sub>2</sub> O <sup>+</sup> (12.89) [971]	1.2 [1.3]	SF <sub>5</sub> <sup>+</sup> (98) SF <sub>4</sub> Cl <sup>+</sup> (2)	Cl + N <sub>2</sub> O F + N <sub>2</sub> O	-55 -31
H <sub>2</sub> O <sup>+</sup> (12.62) [962]	1.7 [1.9]	SF <sub>2</sub> OH <sup>+</sup> (4) SF <sub>3</sub> <sup>+</sup> (2) SF <sub>2</sub> Cl <sup>+</sup> (6) SF <sub>5</sub> <sup>+</sup> (35) SF <sub>4</sub> Cl <sup>+</sup> (53) SF <sub>5</sub> <sup>+</sup> (97) SF <sub>4</sub> Cl <sup>+</sup> (3)	ClF <sub>2</sub> + FH 2 HF + ClO 2 HF + FO Cl + H <sub>2</sub> O FH + OH ClO <sub>2</sub> FO <sub>2</sub>	$\Delta_f H_0^\circ(\text{SF}_2\text{OH}^+)^h - 331^d$ -78 $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+)^e - 431$ -29 -78 <sup>a</sup> 3 -3 <sup>a</sup>
O <sub>2</sub> <sup>+</sup> (12.07) [887]	1.2 [1.5]	SF <sub>5</sub> <sup>+</sup> (97) SF <sub>4</sub> Cl <sup>+</sup> (3)	ClO <sub>2</sub> FO <sub>2</sub>	3 -3 <sup>a</sup>
SF <sub>4</sub> <sup>+</sup> (11.92) [976]	0.3 [1.0]	SF <sub>4</sub> Cl <sup>+</sup> (100)	SF <sub>5</sub>	-91 <sup>a</sup>
CF <sub>2</sub> <sup>+</sup> (11.43) [1122]	1.2 [1.2]	CF <sub>2</sub> Cl <sup>+</sup> (17) SF <sub>5</sub> <sup>+</sup> (14) SF <sub>4</sub> Cl <sup>+</sup> (69)	SF <sub>5</sub> CF <sub>2</sub> Cl CF <sub>3</sub>	-206 -116 -237 <sup>a</sup>
SF <sup>+</sup> (10.25) [1034]	0.8 [1.2]	SF <sub>5</sub> <sup>+</sup> (93) SF <sub>4</sub> Cl <sup>+</sup> (7)	ClSF SF <sub>2</sub>	-77 <sup>i</sup> -149 <sup>a</sup>
SF <sub>2</sub> <sup>+</sup> (10.17) [876]	no reaction			
NO <sub>2</sub> <sup>+</sup> (9.59) [607]	no reaction			
SF <sub>5</sub> <sup>+</sup> (9.55)	0.08 [0.9]	SF <sub>4</sub> Cl <sup>+</sup> (100)	SF <sub>6</sub>	-156 <sup>a</sup>

**Table 2** (continued)

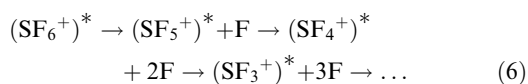
Reagent ion	Rate coefficient/ $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Product ion (%)	Proposed neutral products	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}{}^a$
[1040] NO <sup>+</sup> (9.26)	no reaction			
[797] CF <sup>+</sup> (9.10)	1.5 [1.5]	CF <sub>2</sub> Cl <sup>+</sup> (3) SF <sub>3</sub> <sup>+</sup> (3)	SF <sub>4</sub> CClF <sub>3</sub>	−343 −482
[1066]		SF <sub>5</sub> <sup>+</sup> (27) SF <sub>4</sub> Cl <sup>+</sup> (67)	ClF + CF <sub>2</sub> CClF	−22 −74
CF <sub>3</sub> <sup>+</sup> (9.03)	0.7 [1.1]	SF <sub>5</sub> <sup>+</sup> (39) SF <sub>4</sub> Cl <sup>+</sup> (61)	CF <sub>2</sub> CClF <sub>3</sub>	−181 <sup>a</sup> −43
[1085] SF <sub>3</sub> <sup>+</sup> (8.26)	no reaction		CF <sub>4</sub>	−201 <sup>a</sup>
[870] H <sub>3</sub> O <sup>+</sup> (6.27)	no reaction			
[843]				

<sup>a</sup>  $\Delta_f H_0^\circ(\text{SF}_4\text{Cl}^+) = 150 \text{ kJ mol}^{-1}$ , see text. <sup>b</sup>  $D_0(\text{F-CO}_2) = 48 \text{ kJ mol}^{-1}$  from Arnold *et al.*<sup>39</sup> <sup>c</sup>  $\Delta_f H_0^\circ(\text{SFCI}^+) \sim 782 \text{ kJ mol}^{-1}$ , estimate, see text. <sup>d</sup>  $\Delta_f H_0^\circ(\text{ClF}_2) = -105 \text{ kJ mol}^{-1}$ , from Lias *et al.*<sup>56</sup> <sup>e</sup>  $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+) \sim 453 \text{ kJ mol}^{-1}$ , estimate, see text. <sup>f</sup>  $\Delta_f H_0^\circ(\text{CF}_2\text{O}) = -603 \text{ kJ mol}^{-1}$  from Louis *et al.*<sup>53</sup> <sup>g</sup>  $\Delta_f H_0^\circ(\text{CF}_3\text{O}_2) = -640 \text{ kJ mol}^{-1}$  from Haworth *et al.*<sup>57</sup> <sup>h</sup>  $\Delta_f H_0^\circ(\text{SF}_2\text{OH}^+) \sim 321 \text{ kJ mol}^{-1}$ , estimate, see text. <sup>i</sup> Assuming bond additivity,  $\Delta_f H_0^\circ(\text{ClSF}) = [\Delta_f H_0^\circ(\text{SF}_2) + \Delta_f H_0^\circ(\text{SCl}_2)]/2 = -154 \text{ kJ mol}^{-1}$ .

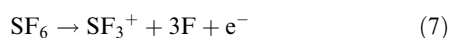
can occur, with smaller product ions possibly resulting from more extensive fragmentation, for example:



Experimental observations of the fragmentation of  $(\text{SF}_6^+)^{*21}$  favour a mechanism with sequential loss of F atoms:<sup>22</sup>



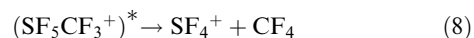
Indeed, the observed threshold for the production of  $\text{SF}_3^+$  from  $\text{SF}_6^{23}$  corresponds closely to the energy needed to access the dissociative ionisation limit:



The dissociation of isolated energy-selected  $(\text{SF}_5\text{CF}_3^+)^*$  ions has been investigated using the TPEPICO (Threshold Photo-Electron PhotoIon COincidence) technique.<sup>10</sup> Making the assumption that the pathway to  $\text{CF}_3^+$  is reaction (1), the experimentally established adiabatic energy for the production of  $\text{CF}_3^+$  ( $12.9 \pm 0.4 \text{ eV}^{10}$ ) can be used as the starting point to build up the adiabatic energies for the production of other ions from  $\text{SF}_5\text{CF}_3$  by dissociative ionisation. The results are displayed in Fig. 1, which was constructed using recently published 0 K enthalpies of formation for  $\text{CF}_m$  and  $\text{CF}_m^+$ ,<sup>24</sup> and for  $\text{SF}_n$  and  $\text{SF}_n^+$ ,<sup>25</sup> obtained from high level *ab initio* calculations.

The predicted lower bounds on the appearance energies for the formation of  $\text{SF}_5^+$ ,  $\text{SF}_4^+$ ,  $\text{SF}_3^+$ , and  $\text{CF}_2^+$  from the pathways (reactions (2) to (5)) listed above are collected in Table 4. These ions have been detected following both photoionisation<sup>10</sup> and electron impact ionisation<sup>26</sup> of  $\text{SF}_5\text{CF}_3$ , and the experimental appearance energies (at 298 K) are presented in Table 4. The appearance energy for  $\text{SF}_5^+$  is entirely consistent with the suggestion that this ion is formed by simple scission of the S–C bond (reaction (2)). However,  $\text{SF}_4^+$ ,  $\text{SF}_3^+$ , and  $\text{CF}_2^+$  all appear at energies well below the predicted thresholds. In order to find energetically accessible pathways

to these fragment ions at their observed appearance energies, it is necessary to postulate more complicated dissociation mechanisms, which involve bond making as well as bond breaking. The lowest energy pathways to  $\text{SF}_4^+$ ,  $\text{SF}_3^+$ , and  $\text{CF}_2^+$  are:



In each case the breaking of the S–C bond is accompanied by migration of F across this bond. One view of the overall process is that reaction (8) corresponds to dissociation (1) followed by F<sup>−</sup> abstraction from  $\text{SF}_5$  by  $\text{CF}_3^+$ , similarly (10) commences with (2). Reactions (8) and (9) may be connected, with excited  $(\text{SF}_4^+)^*$  formed by (8) subsequently fragmenting to produce  $\text{SF}_3^+$ ; the  $\text{SF}_3^+ \text{--F}$  bond is quite weak ( $D_0(\text{SF}_3^+ \text{--F}) = 48 \text{ kJ mol}^{-1}$ ). The predicted threshold energies for  $\text{SF}_4^+$ ,  $\text{SF}_3^+$ , and  $\text{CF}_2^+$  produced through pathways (8), (9), and (10) are given in Table 4. In each case the prediction lies below the experimentally observed appearance energies for these ions. At threshold it is concluded that production of  $\text{SF}_4^+$ ,  $\text{SF}_3^+$ , and  $\text{CF}_2^+$  requires migration of an F atom across the S–C bond. Fig. 1 includes these predicted threshold energies. Also shown are the lowest energy channels to  $\text{SF}_2^+$ ,  $\text{SF}^+$ ,  $\text{S}^+$ ,  $\text{CF}^+$ ,  $\text{F}_2^+$ , and  $\text{F}^+$ , most of these channels involve migration of an F atom across the S–C bond. Many other dissociative ionisation pathways do exist.

When information on the energetics of the dissociative ionisation pathways is combined with the recombination energies of the reagent ions, Fig. 1 provides a visual summary of which product ions are accessible through exothermic charge-transfer pathways for the various reagent ions. The calculated 0 K enthalpy changes of the lowest energy charge-transfer reactions to the observed product ions are given in Table 1. For reagent ions with recombination energies of 12.5 eV or greater, charge transfer provides an exothermic or close to thermoneutral pathway to each of the observed product ions.

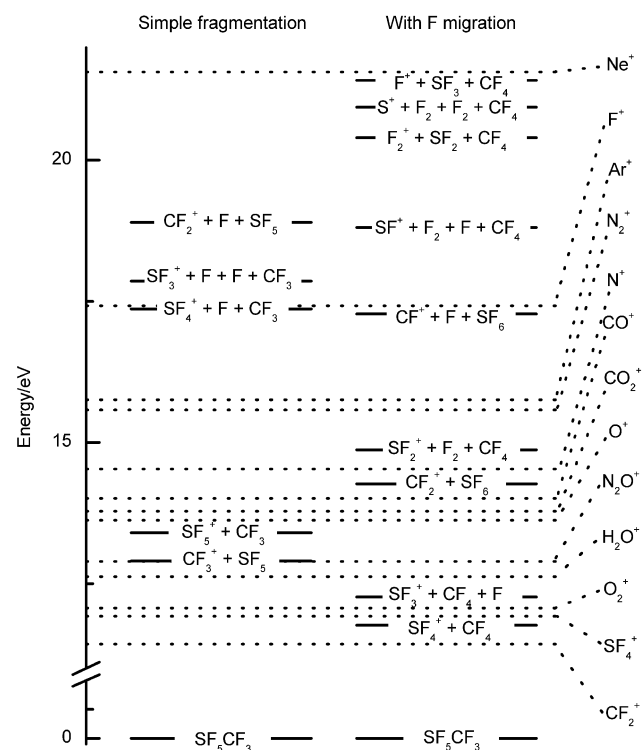
It is frequently instructive to compare the product ion branching ratios observed for a reagent ion of recombination

**Table 3** The measured 300 K reaction rate coefficients (in units of  $10^{-9}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>), cation product ions, their branching ratios (percentages), suggested neutral products and 0 K enthalpies for the reactions of Ne<sup>+</sup>, F<sup>+</sup>, Ar<sup>+</sup>, N<sub>2</sub><sup>+</sup>, N<sup>+</sup>, CO<sup>+</sup>, CO<sub>2</sub><sup>+</sup>, O<sup>+</sup>, N<sub>2</sub>O<sup>+</sup>, H<sub>2</sub>O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, SF<sub>4</sub><sup>+</sup>, CF<sub>2</sub><sup>+</sup>, SF<sup>+</sup>, SF<sub>2</sub><sup>+</sup>, NO<sub>2</sub><sup>+</sup>, SF<sub>5</sub><sup>+</sup>, NO<sup>+</sup>, CF<sup>+</sup>, CF<sub>3</sub><sup>+</sup>, SF<sub>3</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup> with SF<sub>6</sub> are presented. The recombination energies of the reagent cations are listed in eV in brackets under the cations. The value in square brackets is the fluoride affinity of the reagent cation. The capture rate coefficients, calculated using Langevin theory,<sup>19</sup> are presented in square brackets under the experimental values. The measured rate coefficients are considered to be accurate to  $\pm 20\%$ . When dissociative charge transfer is exothermic, only this channel is represented in the table, with the neutrals assembled to give the lowest reaction enthalpy. 0 K enthalpies of formation for CF<sub>m</sub><sup>+</sup>, CF<sub>m</sub>,<sup>24</sup> and for SF<sub>n</sub>, SF<sub>n</sub><sup>+</sup><sup>25</sup> are taken from recent high level *ab initio* calculations. Other 0 K enthalpy data are taken from the JANAF tabulations,<sup>27</sup> information available at the NIST website,<sup>51</sup> and additional sources of data as identified in the table footnotes

Reagent ion	Rate coefficient/ $10^{-9}$ cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	Product ion (%)	Proposed neutral products	$\Delta_f H_0^\circ$ /kJ mol <sup>-1</sup>
Ne <sup>+</sup> (21.56) [1753]	0.69, <sup>a</sup> 0.8 <sup>b</sup> [1.5]	SF <sub>3</sub> <sup>+</sup> (91) <sup>b</sup> SF <sub>4</sub> <sup>+</sup> (3) <sup>b</sup>	F <sub>2</sub> + F + Ne F <sub>2</sub> + Ne	-437 -485
F <sup>+</sup> (17.42) [1508]	1.1 <sup>a</sup> [1.5]	SF <sub>5</sub> <sup>+</sup> (6) <sup>b</sup> SF <sub>3</sub> <sup>+</sup> (10) <sup>a</sup> SF <sub>5</sub> <sup>+</sup> (90) <sup>a</sup>	F + Ne F <sub>2</sub> + F + F F + F	-713 -38 -313
Ar <sup>+</sup> (15.76) [1193]	0.91, <sup>a</sup> 0.93, <sup>c</sup> 1.2 <sup>d</sup> [1.1]	SF <sub>5</sub> <sup>+</sup> (100)	F + Ar	-153
N <sub>2</sub> <sup>+</sup> (15.58) [1175]	1.0, <sup>a</sup> 1.2, <sup>b</sup> 1.3 <sup>d,e</sup> [1.3]	SF <sub>5</sub> <sup>+</sup> (100)	F + N <sub>2</sub>	-135
N <sup>+</sup> (14.53) [1374]	1.8, <sup>b</sup> 1.4 <sup>d,e</sup> [1.7]	SF <sub>3</sub> <sup>+</sup> (2) <sup>b</sup> SF <sub>5</sub> <sup>+</sup> (98) <sup>b</sup>	F <sub>2</sub> + FN F + N	-58 -34
CO <sup>+</sup> (14.01) [1173]	0.92, <sup>a</sup> 1.3, <sup>d</sup> 0.98 <sup>f</sup> [1.3]	SF <sub>5</sub> <sup>+</sup> (100)	CO + F FCO	+16 -133 <sup>g</sup>
CO <sub>2</sub> <sup>+</sup> (13.77) [1049]	0.009, <sup>a</sup> 0.014 <sup>e</sup> [1.1]	SF <sub>5</sub> <sup>+</sup> (100)	F + CO <sub>2</sub> FCO <sub>2</sub>	+39 -10 <sup>h</sup>
O <sup>+</sup> (13.62) [971]	1.5, <sup>d</sup> 2.4 <sup>i</sup> [1.6]	SF <sub>5</sub> <sup>+</sup> (100)	F + O FO	+54 -162
N <sub>2</sub> O <sup>+</sup> (12.89) [971]	0.003 <sup>a</sup> [1.1]	SF <sub>5</sub> <sup>+</sup> (100)	F + N <sub>2</sub> O FO + N <sub>2</sub>	+124 +69
H <sub>2</sub> O <sup>+</sup> (12.6) [962]	0.19 <sup>b</sup> [1.5]	OSF <sub>4</sub> <sup>+</sup> OHSF <sub>5</sub> <sup>+</sup> H <sub>2</sub> OSF <sub>6</sub> <sup>+</sup>	2 HF HF	$\Delta_f H_0^\circ(\text{OSF}_4^+) - 317$ $\Delta_f H_0^\circ(\text{OHSF}_5^+) - 45$ $\Delta_f H_0^\circ(\text{H}_2\text{OSF}_6^+) + 228$
O <sub>2</sub> <sup>+</sup> (12.07) [887]	no reaction <sup>d</sup>			
SF <sub>4</sub> <sup>+</sup> (11.92) [976]	no reaction <sup>j</sup>			
CF <sub>2</sub> <sup>+</sup> (11.43) [1122]	0.79 <sup>a</sup> [1.0]	SF <sub>5</sub> <sup>+</sup> (100)	CF <sub>3</sub>	-82
SF <sup>+</sup> (10.25) [1034]	no reaction <sup>j</sup>			
SF <sub>2</sub> <sup>+</sup> (10.17) [876]	no reaction <sup>j</sup>			
NO <sub>2</sub> <sup>+</sup> (9.59) [607]	no reaction <sup>e</sup>			
SF <sub>5</sub> <sup>+</sup> (9.55) [1040]	no reaction <sup>j</sup>			
NO <sup>+</sup> (9.26) [797]	no reaction <sup>d,e</sup>			
CF <sup>+</sup> (9.10) [1066]	0.88 <sup>a</sup> [1.2]	CF <sub>3</sub> <sup>+</sup> (5) <sup>a</sup> SF <sub>5</sub> <sup>+</sup> (95) <sup>a</sup>	SF <sub>4</sub> CF <sub>2</sub>	-269 -26
CF <sub>3</sub> <sup>+</sup> (9.03) [1085]	0.22, <sup>a</sup> 0.25 <sup>e</sup> [0.9]	SF <sub>5</sub> <sup>+</sup> (100)	CF <sub>4</sub>	-45
SF <sub>3</sub> <sup>+</sup> (8.26)	no reaction <sup>j</sup>			

**Table 3** (continued)

Reagent ion	Rate coefficient/ $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Product ion (%)	Proposed neutral products	$\Delta_f H_0^\circ / \text{kJ mol}^{-1}$
[870] $\text{H}_3\text{O}^+$ (6.27) [843]	no reaction <sup>a</sup>			
<sup>a</sup> Jarvis <i>et al.</i> <sup>8 b</sup> Williams <i>et al.</i> <sup>7 c</sup> Shul <i>et al.</i> <sup>4 d</sup> Fehsenfeld. <sup>1 e</sup> Babcock and Streit. <sup>3 f</sup> Bowers <i>et al.</i> <sup>2 g</sup> $\Delta_f H_0^\circ(\text{FCO}) = -185 \text{ kJ mol}^{-1}$ from Dixon and Feller. <sup>52 h</sup> $D_0(\text{F-CO}_2) = 48 \text{ kJ mol}^{-1}$ , experimental value from Arnold <i>et al.</i> <sup>39 i</sup> Morris <i>et al.</i> <sup>6 j</sup> This study.				



**Fig. 1** Adiabatic dissociative ionisation limits below 22 eV for  $\text{SF}_5\text{CF}_3$ . The limits are divided into those attained by simple fragmentation, and those involving the migration of an F atom across the S-C bond. The recombination energies of the reagent ions with  $\text{RE} > 11 \text{ eV}$  are also presented in the figure. The electrons have been omitted from the labelling of the various limits.

energy  $\text{RE}$  with the TPEPICO ion product branching ratios obtained with photons of energy  $\text{RE}$ . Similar values and trends for branching ratios are regarded as an indicator that the charge-transfer reaction proceeds *via* a long-range mechanism. TPEPICO experiments<sup>10</sup> have shown that the

major product ions from photoionisation of  $\text{SF}_5\text{CF}_3$  are  $\text{CF}_3^+$  and  $\text{SF}_3^+$ , accompanied by small amounts of  $\text{SF}_4^+$ ,  $\text{SF}_5^+$ , and  $\text{CF}_2^+$ . Over the photon energy range 15 to 20 eV, the TPEPICO branching ratios to  $\text{CF}_3^+$  and  $\text{SF}_3^+$  are approximately constant, 70%  $\text{CF}_3^+$  and 20%  $\text{SF}_3^+$ . The product branching ratios for the reactions of  $\text{SF}_5\text{CF}_3$  with  $\text{N}_2^+$ ,  $\text{Ar}^+$ , and  $\text{F}^+$ , presented in Table 1, mirror this behaviour. Above about 20 eV, the TPEPICO branching ratio to  $\text{CF}_3^+$  starts to fall, whilst that to  $\text{SF}_3^+$  rises. The product branching ratios for the reaction of  $\text{Ne}^+$ , compared to  $\text{N}_2^+$ ,  $\text{Ar}^+$ , and  $\text{F}^+$ , with  $\text{SF}_5\text{CF}_3$  display the same trend. The TPEPICO data show two interesting features within the photon energy range 12.7 to 15.5 eV. At about 14.9 eV, there is a rapid increase in the  $\text{SF}_3^+$  branching ratio, from 2% ( $h\nu < 14.8 \text{ eV}$ ) to 20% ( $h\nu > 15 \text{ eV}$ ). This change in dissociation behaviour occurs at the onset of photoionisation into the first excited state of  $\text{SF}_5\text{CF}_3^+$ . In contrast, the product branching ratios show no evidence of a significant change in the yield of  $\text{SF}_3^+$ , which remains at close to 20% as the recombination energy of the reagent ion increases from 12.9 eV to more than 16 eV. Below 13 eV the TPEPICO branching ratio for  $\text{SF}_3^+$  shows a rapid rise, with a matching fall for  $\text{CF}_3^+$ . These observations at around 12.9 eV, the observed thermodynamic limit for the formation of  $\text{CF}_3^+$  by (1), reflect the competition between (1) and (9). Reaction (1) is a simple dissociation, through a loose transition state, while the more complicated mechanism envisaged for (9), requiring intramolecular  $\text{F}^-$  abstraction as well as dissociation, will have a tight transition state. Once (1) opens, the yield of  $\text{SF}_3^+$  (calculated threshold 12.26 eV) rapidly decreases, and  $\text{CF}_3^+$  is the dominant product ion. This may account for the very high  $\text{SF}_3^+$  branching ratio (92%) from the reaction of  $\text{H}_2\text{O}^+$  ( $\text{RE} = 12.61 \text{ eV}$ ) with  $\text{SF}_5\text{CF}_3$ , compared to 19% from the reaction of  $\text{N}_2\text{O}^+$  ( $\text{RE} = 12.89 \text{ eV}$ ). An alternative view<sup>12</sup> is that there is a change in reaction mechanism between  $\text{N}_2\text{O}^+$  and  $\text{H}_2\text{O}^+$ . It is postulated that  $\text{N}_2\text{O}^+$  reacts by charge transfer, leading to  $\text{CF}_3^+$  as the major product. Since the recombination energy of  $\text{H}_2\text{O}^+$  (12.62 eV) is below the observed onset of photoionisation of  $\text{SF}_5\text{CF}_3$  ( $12.9 + 0.2 \text{ eV}^{10}$ ),  $\text{H}_2\text{O}^+$  is unlikely

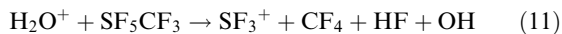
**Table 4** Calculated and observed appearance energies for the dissociative ionisation of  $\text{SF}_5\text{CF}_3$

Fragment ion	Neutral fragment(s)	Reaction	Predicted appearance energy/eV	Observed appearance energy/eV	
				Photoionisation (TPEPICO) <sup>10</sup>	Electron impact ionisation <sup>26</sup>
$\text{CF}_3^+$	$\text{SF}_5$	(1)	12.9 <sup>a</sup>	$12.9 \pm 0.4$	$12.9 \pm 0.1$
$\text{SF}_5^+$	$\text{CF}_3$	(2)	13.40	$13.9 \pm 1.5$	$13.2 \pm 0.6$
$\text{CF}_2^+$	$\text{F} + \text{SF}_5$	(3)	18.90		
	$\text{SF}_6$	(10)	14.27	$16.0 \pm 2.0$	$17.8 \pm 0.5$
$\text{SF}_4^+$	$\text{F} + \text{CF}_3$	(4)	17.37		
	$\text{CF}_4$	(8)	11.76	$13.5 \pm 1.5$	$12.1 \pm 0.3$
$\text{SF}_3^+$	$\text{F} + \text{F} + \text{CF}_3$	(5)	17.86		
	$\text{F} + \text{CF}_4$	(9)	12.26	$14.94 \pm 0.13$	$14.5 \pm 0.1$

<sup>a</sup> Obtained from the TPEPICO study.<sup>10</sup>



to react efficiently by charge transfer, and instead a chemical pathway in which bonds are broken and formed leads to the major product:



It is difficult to discern trends in the small TPEPICO branching ratios to  $\text{SF}_5^+$ ,  $\text{SF}_4^+$ , and  $\text{CF}_2^+$ , but it does appear that the yield of  $\text{SF}_5^+$  increases with photon energy. The charge-transfer data show that the reactions produce an increasing proportion of  $\text{SF}_5^+$  as the recombination energy of the reagent ion increases. This can be viewed as a consequence of competition between channels (1) and (2). As the available energy increases, the dissociation of  $(\text{SF}_5\text{CF}_3)^+$  produces a greater proportion of  $\text{SF}_5^+$  (thermodynamic threshold 13.40 eV) compared to  $\text{CF}_3^+$  (12.90 eV).

In addition to product ion branching ratios, the reaction rate coefficient can be a useful diagnostic of the mechanism. For long-range charge-transfer to be efficient, identified by  $k_{\text{exp}}/k_{\text{c}} \sim 1$ , it is necessary that there is good vibrational overlap between the neutral reactant M and the ion  $(\text{M}^+)^*$  initially formed by charge transfer:

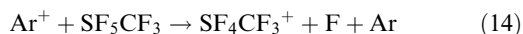


This can be judged by inspecting the photoelectron spectrum of M. For the generic charge-transfer reaction (12), energy balance requires that:

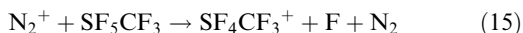
$$E[(\text{M}^+)^*] - E(\text{M}) = \text{RE}(\text{A}^+) \quad (13)$$

so if there is a strong signal in the photoelectron spectrum of M at an ionisation energy equal to  $\text{RE}(\text{A}^+)$ , efficient charge-transfer (reaction (12)) can be anticipated. The photoelectron spectrum of  $\text{SF}_5\text{CF}_3$  has not been reported. However, a TPES (Threshold PhotoElectron Spectrum) of  $\text{SF}_5\text{CF}_3$  is available.<sup>10</sup> It shows a significant yield of electrons for all photon energies from 12.5 eV to greater than 23 eV. This suggests that if the mechanism of reaction for all reagent ions with recombination energies greater than 12.5 eV is long-range charge-transfer, then the reactions should all be efficient. This is confirmed by the data in Table 1. The combination of reaction rate coefficients equal to the capture estimates, and product ion yields matching TPEPICO results confirms that the reactions of  $\text{SF}_5\text{CF}_3$  with reagent ions possessing recombination energies greater than 12.5 eV can be viewed as long-range charge transfer reactions.

The reactions with  $\text{Ar}^+$  and  $\text{N}_2^+$  resulted in one product ion not observed from other charge-transfer reactions. This product ion has a mass of 177 u, and could be either  $\text{SF}_4\text{CF}_3^+$  or  $\text{SF}_5\text{CF}_2^+$  (or both). Since the bond dissociation energy of S–F in  $\text{SF}_6$  is less than that of C–F in  $\text{CF}_4$ , we propose that  $\text{SF}_4\text{CF}_3^+$  is the product ion.  $\text{SF}_4\text{CF}_3^+$  (and/or  $\text{SF}_5\text{CF}_2^+$ ) was not a reported product of either the electron impact ionisation<sup>26</sup> or the photoionisation of  $\text{SF}_5\text{CF}_3$ .<sup>10</sup> The observation of the charge-transfer reactions:



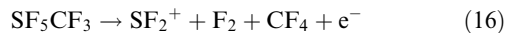
and



can be used to estimate an upper bound for the enthalpy of formation of  $\text{SF}_4\text{CF}_3^+$ ,  $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+)$ . However, the possibility that the  $\text{Ar}^+$  ( $^2\text{P}_{1/2}$  and  $^2\text{P}_{3/2}$ ) and  $\text{N}_2^+$  ( $v = 1$  and 0) reagent ions may not be fully thermalised increases the uncertainty in the estimate. If the  $\text{SF}_4\text{CF}_3^+$ , for which the branching ratio is only 1 or 2%, is formed from the reactions of  $\text{Ar}^+$  ( $^2\text{P}_{1/2}$ ) and  $\text{N}_2^+$  ( $v = 1$ ), then the bound obtained is  $< -221 \text{ kJ mol}^{-1}$ , while if this ion can be formed from  $\text{Ar}^+$  ( $^2\text{P}_{3/2}$ ) and  $\text{N}_2^+$  ( $v = 0$ ), then the bound is  $< -247 \text{ kJ mol}^{-1}$ . These limits use a value for  $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3) = -1673 \text{ kJ mol}^{-1}$ , obtained by

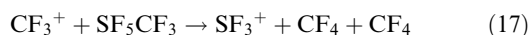
combining the TPEPICO determination of the dissociative ionisation limit for reaction (1), with the enthalpies of formation for  $\text{CF}_3^{+24}$  and  $\text{SF}_5^{25}$  obtained from recent *ab initio* calculations. The failure to observe  $\text{SF}_4\text{CF}_3^+$  as a product of the reaction of  $\text{N}^+$  with  $\text{SF}_5\text{CF}_3$  provides a tentative lower bound  $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+) > -348 \text{ kJ mol}^{-1}$ .

The product ion mass spectra were carefully inspected for the presence of  $\text{SF}_2^+$ , which has a mass only 1 u greater than that of  $\text{CF}_3^+$ . The lowest energy dissociative ionisation pathway to  $\text{SF}_2^+$  is:

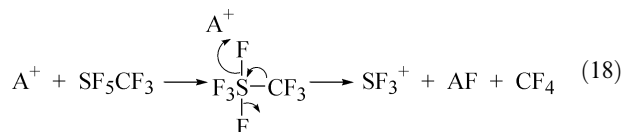


for which the thermodynamic limit is 14.87 eV.  $\text{SF}_2^+$  was only observed as a product of the reaction of  $\text{SF}_5\text{CF}_3$  with  $\text{Ne}^+$ . It was not seen in the TPEPICO spectra of  $\text{SF}_5\text{CF}_3$ .

Inspection of Table 1 shows that there are reactions between  $\text{SF}_5\text{CF}_3$  and certain reagent ions whose recombination energies are below the calculated adiabatic threshold for the lowest energy dissociative ionisation channel of  $\text{SF}_5\text{CF}_3$  ( $\rightarrow \text{SF}_4^+ + \text{CF}_4 + \text{e}^-$ , 11.76 eV). An example is the reaction between  $\text{CF}_3^+$  and  $\text{SF}_5\text{CF}_3$ :



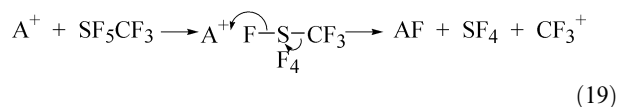
(this is the most exothermic pathway to  $\text{SF}_3^+$  from these reactants). In contrast to the charge-transfer reactions (12), where there is no exchange of atoms between A and M, and A is a spectator to the dissociation of  $(\text{M}^+)^*$ , the pathway to these proposed products involves the formation of a new chemical bond between the reagent ion ( $\text{CF}_3^+$ ) and a fragment abstracted from  $\text{SF}_5\text{CF}_3$  ( $\text{F}^-$ ). For the reaction above this is coupled with fragmentation of  $\text{SF}_4\text{CF}_3^+$  to release the observed ion product  $\text{SF}_3^+$ . Since  $\text{SF}_4\text{CF}_3^+$  is not observed as a product of the reaction (which is consistent with the proposed bounds on  $\Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+)$ ), the overall reaction may well be concerted:



( $\text{CF}_3^+$  has been replaced by the generic reagent ion  $\text{A}^+$ , because we believe the several other reactions in which  $\text{SF}_3^+$  is formed proceed *via* this mechanism, see below)

The reactions of  $\text{SF}_5\text{CF}_3$  do not furnish any examples of detected ion products which contain new bonds between units from  $\text{SF}_5\text{CF}_3$  and the reagent ion. The existence of pathways such as (18) is inferred from the requirement that the overall proposed reaction must be close to thermoneutral or exothermic, in order for it to proceed at an observable rate. The reactions of  $\text{SF}_5\text{CF}_3$  with  $\text{SF}_4^+$ ,  $\text{CF}_2^+$ ,  $\text{SF}^+$ ,  $\text{SF}_5^+$ ,  $\text{CF}^+$ , and  $\text{CF}_3^+$  provide further examples of reactions proceeding *via* chemical rather than charge-transfer pathways. Table 1 indicates the likely neutral products, identified from the exothermicity criterion. For all of the reactions,  $\text{SF}_3^+$  is one of the major product ions, and the inferred product neutrals point to reaction *via* mechanism (18). A more exothermic pathway exists for the reaction with  $\text{CF}^+$ , with  $\text{C}_2\text{F}_6$  as the neutral product, rather than  $\text{CF}_2 + \text{CF}_4$  as anticipated for reaction (18).

The other major product ion seen from the reactions of  $\text{CF}_2^+$ ,  $\text{SF}^+$ ,  $\text{SF}_5^+$ , and  $\text{CF}^+$  is  $\text{CF}_3^+$ , and reaction (19) shows a possible mechanism:



As Table 1 shows, for both  $\text{CF}_2^+$  and  $\text{CF}^+$  there is a more exothermic route to  $\text{CF}_3^+$ , with  $\text{CF}_4$  as one of the neutral products. The lowest energy pathways to  $\text{CF}_3^+$  from the reactions of  $\text{SF}_4^+$ ,  $\text{SF}_2^+$ , and  $\text{SF}_3^+$  have substantial endothermicities,

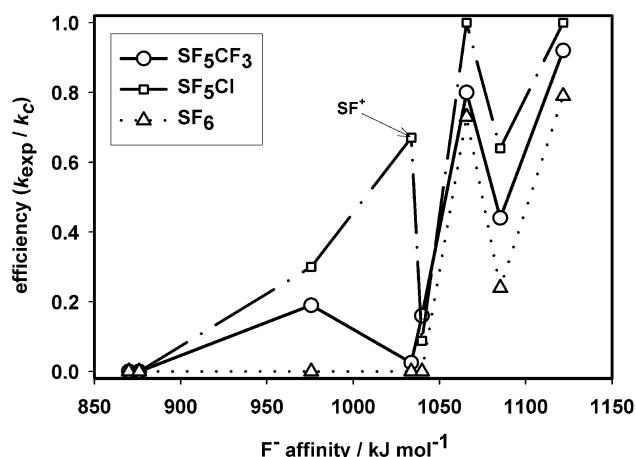


Fig. 2 Plot of reaction efficiencies ( $k_{\text{exp}}/k_c$ ) against fluoride ion affinity for the reactions of the  $\text{CF}_m^+$  ( $m = 1-3$ ) and  $\text{SF}_n^+$  ( $n = 1-5$ ) reagent ions with  $\text{SF}_5\text{CF}_3$ ,  $\text{SF}_5\text{Cl}$ , and  $\text{SF}_6$ .

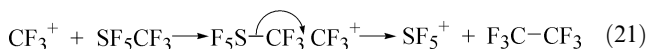
which accounts for the non-observation of  $\text{CF}_3^+$  as a product of any of these reactions.

Reaction schemes (18) and (19) involve the abstraction of  $\text{F}^-$  from  $\text{SF}_5\text{CF}_3$  by the reagent ion, so some correlation of the reaction efficiencies with the  $\text{F}^-$  affinities of the reagent ions can be anticipated. The fluoride affinities of the reagent ions, expressed as minus the 0 K enthalpy change for the reaction:



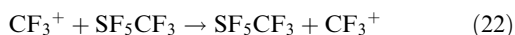
are given in Table 1. The reaction efficiencies are plotted against fluoride affinities in Fig. 2. Comparing the  $\text{CF}_m^+$  ( $m = 1-3$ ) and  $\text{SF}_n^+$  ( $n = 1-5$ ) reagent ions, the  $\text{CF}_m^+$  ions have higher fluoride affinities, and react more efficiently. For  $\text{CF}_2^+$ , which has the highest fluoride affinity,  $\text{F}^-$  abstraction is directly observed, through the identification of  $\text{SF}_4\text{CF}_3^+$  as one of the product ions.

$\text{SF}_5^+$  was identified as a product of the reactions of  $\text{CF}_2^+$ ,  $\text{CF}^+$ , and  $\text{CF}_3^+$  with  $\text{SF}_5\text{CF}_3$ . For  $\text{CF}_2^+$  and  $\text{CF}_3^+$ , the most likely reaction pathway is  $\text{CF}_3^-$  abstraction:



However, a more complicated pathway is required for  $\text{CF}^+$ , because in order to satisfy the exothermicity criterion, the neutral product must be  $\text{CF}_2=\text{CF}_2$ , and not  $\text{CF}-\text{CF}_3$ . Despite this, the  $\text{SF}_5^+$  branching ratio from  $\text{CF}^+ + \text{SF}_5\text{CF}_3$  is about the same (2%) as for the reactions of  $\text{CF}_2^+$  and  $\text{CF}_3^+$ .

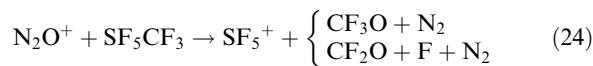
Some confirmation of the proposed mechanisms for the reactions of  $\text{CF}_m^+$  and  $\text{SF}_n^+$  could be obtained by studying the reactions of the isotopically labelled reagent ions,  $^{13}\text{CF}_m^+$  and  $^{34}\text{SF}_n^+$ . Thus reaction scheme (19) predicts that the  $\text{CF}_3^+$  product will not incorporate the  $^{13}\text{C}$  present in labelled  $^{13}\text{CF}_m^+$  reagent ions, and according to scheme (18) the use of labelled  $^{34}\text{SF}_n^+$  will not lead to the production of  $^{34}\text{SF}_3^+$ .  $\text{CF}_3^+$  may undergo two reactions, which are not listed in Table 1, because they do not consume  $\text{CF}_3^+$ :



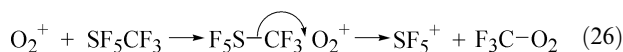
The occurrence of these reactions would be revealed through the use of labelled  $^{13}\text{CF}_3^+$  as the reagent ion.

In accord with the observation that  $\text{NO}^+$  and  $\text{NO}_2^+$  do not react with  $\text{SF}_5\text{CF}_3$ , a search of the possible ion-molecule reactions failed to identify any exothermic reactions. Since  $\text{H}_3\text{O}^+$  does not react with  $\text{SF}_5\text{CF}_3$ , it is concluded that the proton affinity of  $\text{SF}_5\text{CF}_3$  is less than that of  $\text{H}_2\text{O}$ .

For reagent ions with recombination energies greater than 12.5 eV, there is only one case where it is necessary to invoke a chemical pathway to obtain an exothermic reaction to one of the observed ion products. This is:



For  $\text{O}_2^+$ , given the large uncertainty in the dissociative ionisation energy of  $\text{SF}_5\text{CF}_3$ , it is not possible to be certain as to which pathways are exothermic. The situation is further complicated by the likely presence of vibrationally excited  $\text{O}_2^+$ . However, plots of  $\ln(\text{O}_2^+ \text{ counts})$  against  $\text{SF}_5\text{CF}_3$  concentration show no curvature, indicating that the rate coefficient is the same for  $\text{O}_2^+$  in  $v = 0, 1$ , and 2. For  $\text{O}_2^+$  the production of  $\text{CF}_3^+$  and  $\text{SF}_5^+$  is likely to be *via* chemical routes:



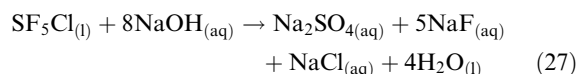
(reaction (26) is  $\text{CF}_3^-$  abstraction, analogous to (21)), with  $\text{SF}_4^+$  coming from a dissociative charge-transfer reaction (8).

Surveying the thermochemistry in Table 1, for which the major source of uncertainty is  $\pm 0.4$  eV ( $\pm 39$  kJ mol $^{-1}$ ) in the dissociative ionisation energy of  $\text{SF}_5\text{CF}_3$  (reaction (1)), shows that all of the observed products can be formed in reactions which are close to thermoneutral or exothermic. Thus application of the exothermicity criterion indicates that there are no obvious inconsistencies in the thermochemical data used in the construction of Table 1. By combining the dissociative ionisation energy of  $\text{SF}_5\text{CF}_3$ <sup>10</sup> with the *ab initio* values for  $\Delta_f H_0^\circ(\text{CF}_3^+)$ ,  $\Delta_f H_0^\circ(\text{CF}_3)$ ,<sup>24</sup> and  $\Delta_f H_0^\circ(\text{SF}_5^+)$ ,<sup>25</sup> the following thermochemical data for  $\text{SF}_5\text{CF}_3$  are obtained:  $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3) = -1673$  kJ mol $^{-1}$  and  $D_0(\text{SF}_5-\text{CF}_3) = 374$  kJ mol $^{-1}$ .

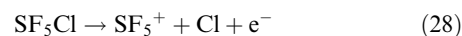
### 3.2 $\text{SF}_5\text{Cl}$ reactions

The experimental reaction rate coefficients for the reactions of  $\text{SF}_5\text{Cl}$  with  $\text{Ne}^+$ ,  $\text{F}^+$ ,  $\text{Ar}^+$ ,  $\text{N}_2^+$ ,  $\text{N}^+$ ,  $\text{CO}^+$ ,  $\text{CO}_2^+$ ,  $\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{O}_2^+$ ,  $\text{SF}_4^+$ ,  $\text{CF}_2^+$ ,  $\text{SF}^+$ ,  $\text{SF}_2^+$ ,  $\text{NO}_2^+$ ,  $\text{SF}_5^+$ ,  $\text{NO}^+$ ,  $\text{CF}^+$ ,  $\text{CF}_3^+$ ,  $\text{SF}_3^+$ , and  $\text{H}_3\text{O}^+$ , together with the observed product ions, and their branching ratios are given in Table 2. Before discussing these results, some basic thermochemistry needs to be evaluated.

The JANAF tables<sup>27</sup> provide a value for the enthalpy of formation of  $\text{SF}_5\text{Cl}$  ( $\Delta_f H_0^\circ(\text{SF}_5\text{Cl}) = -1026$  kJ mol $^{-1}$ ) derived from a thermochemical study of the reaction:<sup>28</sup>



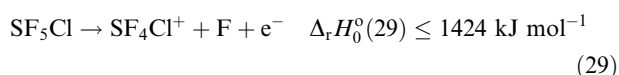
When this is combined with the enthalpy of formation of  $\text{SF}_5^+$  obtained from the high level *ab initio* calculations of Bauschlicher and Ricca,<sup>25</sup> the 0 K adiabatic energy for the lowest dissociative ionisation limit of  $\text{SF}_5\text{Cl}$ :



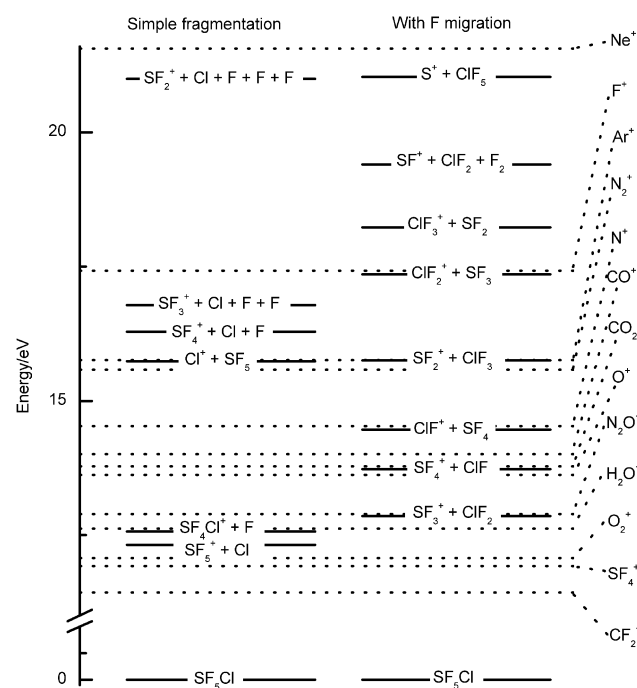
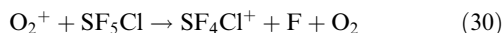
is predicted to be 1230 kJ mol $^{-1}$  or 12.75 eV. This is not consistent with the reported photoionisation data for  $\text{SF}_5\text{Cl}$ . The photoelectron spectrum of  $\text{SF}_5\text{Cl}$ <sup>29</sup> places an upper bound on the adiabatic ionisation energy of  $\text{SF}_5\text{Cl}$  of 12.33 eV. Further, the photoionisation mass spectrum (PIMS) of  $\text{SF}_5\text{Cl}$ <sup>30</sup> shows an onset for the formation of  $\text{SF}_5^+$  of 12.32 eV, with other fragment ions appearing at higher energies. It seems that either  $\Delta_f H_0^\circ(\text{SF}_5\text{Cl})$  or  $\Delta_f H_0^\circ(\text{SF}_5^+)$  must be wrong. Recent years have seen considerable efforts, both experimental and theoretical, to establish a reliable value for  $\Delta_f H_0^\circ(\text{SF}_5^+)$ . A recommended experimental value due to Fisher *et al.*<sup>31</sup> of 11 kJ mol $^{-1}$  would

place the dissociative ionisation limit (28) at 11.99 eV, and give consistency with the observed upper bound to this limit of 12.32 eV. However, theoretical calculations<sup>25,32,33</sup> consistently give rather larger values, for example  $\Delta_f H_0^0(\text{SF}_5^+) = 84 \text{ kJ mol}^{-1}$ ,<sup>25</sup> and some potential problems in the experimental determination of  $\Delta_f H_0^0(\text{SF}_5^+)$  have been identified.<sup>34</sup> In the absence of an independent test of  $\Delta_f H_0^0(\text{SF}_5\text{Cl})$ , and the need to use a consistent set of thermochemistry for  $\text{SF}_5\text{Cl}$ ,  $\text{SF}_n$  and  $\text{SF}_n^+$ , we have chosen to use the observed onset for the dissociative ionisation (28) combined with  $\Delta_f H_0^0(\text{SF}_5^+) = 84 \text{ kJ mol}^{-1}$ ,<sup>25</sup> to determine a lower limit to  $\Delta_f H_0^0(\text{SF}_5\text{Cl}) \geq -985 \text{ kJ mol}^{-1}$ . With the exception that this value is a lower limit, the procedure matches that adopted to determine  $\Delta_f H_0^0(\text{SF}_5\text{CF}_3)$ . In Table 2 and the remainder of the text, we have used  $\Delta_f H_0^0(\text{SF}_5\text{Cl}) = -985 \text{ kJ mol}^{-1}$ . Calculated reaction enthalpies are thus upper bounds. When the revised value for  $\Delta_f H_0^0(\text{SF}_5\text{Cl})$  is combined with thermochemistry for  $\text{SF}_n$  and  $\text{SF}_n^+$  from the *ab initio* calculations of Bauschlicher and Ricca,<sup>25</sup> and for other neutrals and ions from the JANAF tables,<sup>27</sup> Fig. 3, showing the relative energies of many of the lower dissociative ionisation limits of  $\text{SF}_5\text{Cl}$ , can be constructed.

$\text{SF}_4\text{Cl}^+$  is a product of many of the ion-molecule reactions of  $\text{SF}_5\text{Cl}$ , so in analysing the reactions it would be useful to have a value for  $\Delta_f H_0^0(\text{SF}_4\text{Cl}^+)$ .  $\text{SF}_4\text{Cl}^+$  is seen in the electron impact mass spectrum of  $\text{SF}_5\text{Cl}$ ,<sup>35</sup> with an appearance energy of 15.9 eV, and is known to be a product of the dissociative photoionisation of  $\text{SF}_5\text{Cl}$ ,<sup>30,36</sup> the ion is first observed at a photon energy of 14.76 eV. This places an upper bound on the energy for:

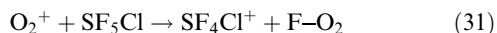


The exothermicity criterion ( $\Delta_r H_0^0 < 0$  for an observed reaction) can be applied to refine the upper bound to  $\Delta_r H_0^0(29)$ . In particular, the observation of  $\text{SF}_4\text{Cl}^+$  from the reaction of  $\text{O}_2^+$  with  $\text{SF}_5\text{Cl}$  produces the lowest upper bound. If the pathway to  $\text{SF}_4\text{Cl}^+$  is through dissociative charge transfer:



**Fig. 3** Adiabatic dissociative ionisation limits below 22 eV for  $\text{SF}_5\text{Cl}$ . The limits are divided into those attained by simple fragmentation, and those involving the migration of an F atom across the S–Cl bond. The recombination energies of the reagent ions with  $\text{RE} > 12 \text{ eV}$  are also presented in the figure. The electrons have been omitted from the labelling of the various limits.

then  $\Delta_r H_0^0(29) < 1165 \text{ kJ mol}^{-1}$ . The other possible route is  $\text{F}^-$  abstraction by  $\text{O}_2^+$ :

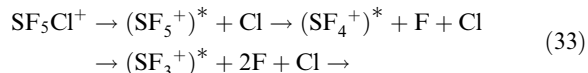


taking  $D_0(\text{F-O}_2) = 50 \text{ kJ mol}^{-1}$ <sup>27</sup> leads to  $\Delta_r H_0^0(29) < 1215 \text{ kJ mol}^{-1}$ . These bounds assume that  $\text{SF}_4\text{Cl}^+$  can be formed from  $\text{O}_2^+(v=0)$ . The neutral products,  $\text{F} + \text{O}_2$  or  $\text{FO}_2$ , are unknown, so other data must be used to choose between these two bounds. The bond dissociation energy  $D_0(\text{SF}_4^+-\text{F})$  is  $383 \text{ kJ mol}^{-1}$ ,<sup>25</sup> it is expected that  $D_0(\text{SF}_4^+-\text{Cl})$  will be lower. Adopting  $\Delta_r H_0^0(29) < 1215 \text{ kJ mol}^{-1}$  gives  $D_0(\text{SF}_4^+-\text{Cl}) > 356 \text{ kJ mol}^{-1}$ , which is reasonable, while  $\Delta_r H_0^0(29) < 1165 \text{ kJ mol}^{-1}$  leads to  $D_0(\text{SF}_4^+-\text{Cl}) > 406 \text{ kJ mol}^{-1}$ . At the onset of photoionisation (12.32 eV) the only observed ion product is  $\text{SF}_5^{+30}$  (reaction 28), a value for  $\Delta_r H_0^0(29)$  below  $1189 \text{ kJ mol}^{-1}$  is then unlikely to be correct. The recommended bound is thus  $\Delta_r H_0^0(29) < 1215 \text{ kJ mol}^{-1}$ , and the value is expected to be quite close to this upper bound. The calculation of the 0 K enthalpy changes for ion-molecule reactions is facilitated by combining  $\Delta_r H_0^0(29)$  with  $\Delta_r H_0^0(\text{SF}_5\text{Cl}) = -985 \text{ kJ mol}^{-1}$ , to give  $\Delta_r H_0^0(\text{SF}_4\text{Cl}^+) < 152 \text{ kJ mol}^{-1}$ ; the calculations shown in Table 2 used  $\Delta_r H_0^0(\text{SF}_4\text{Cl}^+) = 150 \text{ kJ mol}^{-1}$ . Since  $\text{SF}_4\text{Cl}^+$  is a minor product of the reaction between  $\text{O}_2^+$  and  $\text{SF}_5\text{Cl}$ , it could be formed exclusively from the vibrationally excited  $\text{O}_2^+$  known to be present. For example, if all the  $\text{SF}_4\text{Cl}^+$  is produced by the reaction of  $\text{O}_2^+(v=2)$  with  $\text{SF}_5\text{Cl}$ :

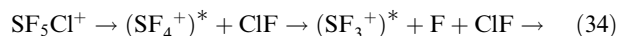


then  $\Delta_r H_0^0(29) < 1259 \text{ kJ mol}^{-1}$ ,  $D_0(\text{SF}_4^+-\text{Cl}) > 312 \text{ kJ mol}^{-1}$ , and  $\Delta_r H_0^0(\text{SF}_4\text{Cl}^+) < 197 \text{ kJ mol}^{-1}$ . This rather higher upper bound for  $\Delta_r H_0^0(29)$  is not ruled out by application of the exothermicity criterion to any of the other reactions observed to form  $\text{SF}_4\text{Cl}^+$ .

$\text{SF}_4^+$  and  $\text{SF}_3^+$  are observed as products of the photoionisation of  $\text{SF}_5\text{Cl}$ ,<sup>30</sup> with appearance energies of 15.87 and 16.2 eV, respectively. Some preliminary work on the TPEPICO spectrum of  $\text{SF}_5\text{Cl}$ <sup>36</sup> gives slightly higher values (at 298 K) of  $16.2 \pm 0.3$  and  $16.8 \pm 0.3 \text{ eV}$ , respectively.  $\text{SF}_4^+$  and  $\text{SF}_3^+$  are observed in the electron impact mass spectrum of  $\text{SF}_5\text{Cl}$ ,<sup>35</sup> but their appearance energies have not been reported. The fragmentation of  $\text{SF}_5\text{Cl}^+$  may occur by step-wise loss of Cl and F atoms:

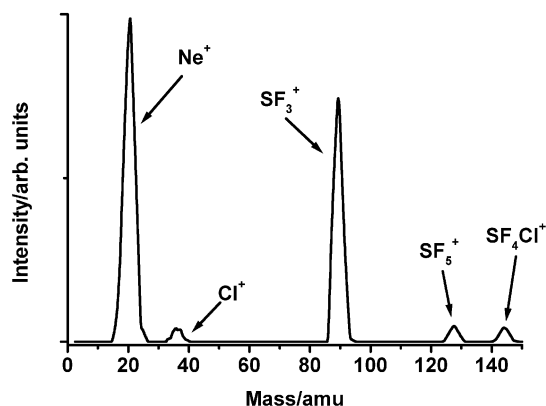


in which case the adiabatic limits to  $\text{SF}_4^+$  and  $\text{SF}_3^+$  will be 16.28 and 16.78 eV, respectively. The other possibility is a concerted fragmentation leading to the formation of  $\text{ClF}$ :



the predicted limits are now 13.72 eV ( $\text{SF}_4^+$ ) and 14.22 eV ( $\text{SF}_3^+$ ). The limit for  $\text{SF}_3^+$  could be even lower, if  $\text{ClF}_2^+$  is formed as the neutral product. The fragment ions  $\text{SF}_4^+$  and  $\text{SF}_3^+$  are not observed at energies well below the limits for their formation by step-wise loss of Cl and F from  $\text{SF}_5\text{Cl}^+$  (reaction scheme (33)). Indeed the preliminary TPEPICO data suggest that their appearance may coincide with the adiabatic energies for simple fragmentation.

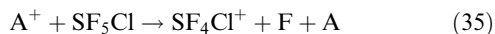
Ion product branching ratio comparisons between the ion-molecule reactions (Table 2) and preliminary results from a TPEPICO study of energy selected  $\text{SF}_5\text{Cl}^{+36} provide strong evidence that the reactions of  $\text{SF}_5\text{Cl}$  with  $\text{Ne}^+$ ,  $\text{F}^+$ ,  $\text{Ar}^+$ , and  $\text{N}_2^+$  all occur *via* long-range charge transfer.<sup>38</sup> Fig. 4 shows the mass spectrum obtained for the reaction of  $\text{Ne}^+$  with  $\text{SF}_5\text{Cl}$ . A large amount of energy (9.25 eV, relative to the lowest dissociative ionisation limit to  $\text{SF}_5^+ + \text{Cl}$ ) is available to dissociate  $(\text{SF}_5\text{Cl}^+)^*$ , and this is reflected in the range of pro-$



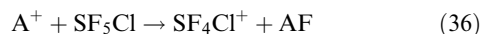
**Fig. 4** A typical mass spectrum obtained from the charge-transfer reaction of  $\text{Ne}^+$  with  $\text{SF}_5\text{Cl}$ , illustrating the considerable degree of fragmentation, that results from the high recombination energy of  $\text{Ne}^+$  (21.56 eV) compared to the other reagent ions used in this study. Four product ions are identified in the figure;  $\text{Cl}^+$ ,  $\text{SF}_3^+$  (dominant),  $\text{SF}_5^+$  and  $\text{SF}_4\text{Cl}^+$ .  $\text{SF}_2^+$  and  $\text{SF}_4^+$  are also observed products of the reaction, but their branching ratios are very small, resulting in product ion intensities which are too small to be discernible on the figure.

duct fragment ions seen in the mass spectrum. Indeed,  $\text{Cl}^+$  and  $\text{SF}_2^+$  are only observed from the reaction of  $\text{SF}_5\text{Cl}$  with  $\text{Ne}^+$ .

For photon energies below 14.8 eV, the only product ion observed in the TPEPICO experiments is  $\text{SF}_5^+$ . The results in Table 2 show that the reactions of  $\text{SF}_5\text{Cl}$  with ions having recombination energies in the range 12.3 to 14.8 eV are efficient, but yield various ion products in addition to  $\text{SF}_5^+$ .  $\text{SF}_4\text{Cl}^+$  is a product of all these reactions. It could be the product of charge transfer and fragmentation, induced by short-range interactions:

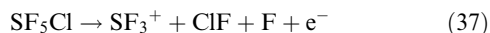


and/or the formation of  $\text{SF}_4\text{Cl}^+$  may be linked to chemical reaction between F and A, such as:

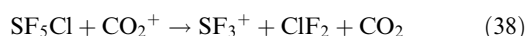


Either (or both) of reactions (35) and (36) may occur when  $\text{RE}(\text{A}^+) > \Delta_f H_0^\circ(29)$ , schemes of the type shown in reaction (36) will be necessary when  $\text{RE}(\text{A}^+) < \Delta_f H_0^\circ(29)$ . The relative branching ratios for  $\text{SF}_5^+$  and  $\text{SF}_4\text{Cl}^+$  vary widely with the reagent ion. There is no correlation of the  $\text{SF}_5^+/\text{SF}_4\text{Cl}^+$  ratio with either the recombination energies of the reagent ions, or with the enthalpies of reactions in which bonds are formed and broken. Specific short-range interactions within the initially formed ion-molecule complex are evidently important to the outcome of the reactions. Without further information, particularly the identification of the neutral products, the mechanisms of the reactions must remain uncertain.

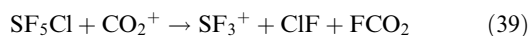
The reaction of  $\text{CO}_2^+$  with  $\text{SF}_5\text{Cl}$  produces a number of interesting products. The recombination energy of  $\text{CO}_2^+$  (13.77 eV) is well below the minimum energy (14.22 eV) required for the dissociative ionisation:



$\Delta_f H_0^\circ(37) - \text{RE}(\text{CO}_2^+) = 43 \text{ kJ mol}^{-1}$ , but  $\text{SF}_3^+$  is an observed (trace) product from the reaction of  $\text{CO}_2^+$ . Two possible routes to  $\text{SF}_3^+$  are dissociative charge transfer with  $\text{ClF}_2$  as the neutral product:



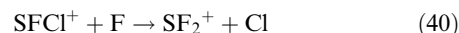
and  $\text{F}^-$  abstraction by  $\text{CO}_2^+$  coupled with fragmentation of the intermediate  $\text{SF}_4\text{Cl}^+$ :



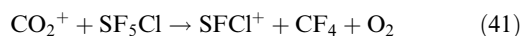
$\text{ClF}_2$  is a stable species, with  $D_0(\text{FCl}-\text{F})$  calculated to lie

between 75 and 133  $\text{kJ mol}^{-1}$ .<sup>37</sup> An experimental determination of  $D_0(\text{F}-\text{CO}_2)$  has yielded a value of 48  $\text{kJ mol}^{-1}$ ,<sup>39</sup> with calculations providing a slightly higher value of 61  $\text{kJ mol}^{-1}$ .<sup>40–42</sup> Thus (38) and (39) are both exothermic routes to  $\text{SF}_3^+$ , and both involve the formation of a relatively weakly bound product neutral.

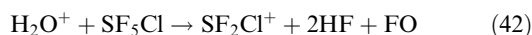
The  $\text{CO}_2^+$  reaction generates two ion products, in addition to  $\text{SF}_4\text{Cl}^+$ , for which enthalpies of formation have not been reported. They are  $\text{SFCl}^+$  and  $\text{SF}_2\text{Cl}^+$ , but it should be noted that only traces of  $\text{SF}_2\text{Cl}^+$  were observed. Estimates of their enthalpies of formation can be obtained, starting from the calculated thermochemistry<sup>25</sup> of  $\text{SF}_2^+$  and  $\text{SF}_3^+$ , and the knowledge that S–Cl bonds are weaker than S–F bonds (for example  $D_0(\text{SF}_5-\text{F}) > D_0(\text{SF}_5-\text{Cl})$ , and  $D_0(\text{S}-\text{F}) > D_0(\text{S}-\text{Cl})$ ). Assuming that for the exchange reaction:



$\Delta_f H_0^\circ = -50 \text{ kJ mol}^{-1}$ , we obtain  $\Delta_f H_0^\circ(\text{SFCl}^+) = 782 \text{ kJ mol}^{-1}$ , which is compatible with the bound of  $\Delta_f H_0^\circ(\text{SFCl}^+) < 878 \text{ kJ mol}^{-1}$ , implied by the observation of the reaction:



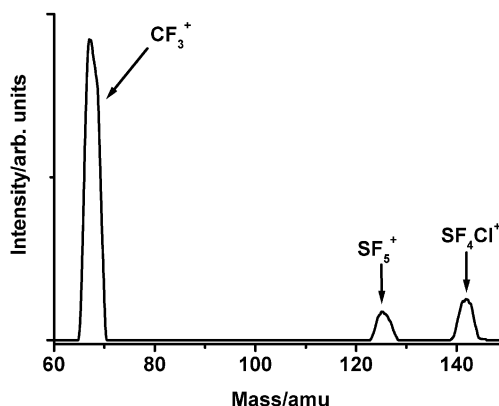
(other neutral products can be excluded, for pathways leading to them cannot satisfy the exothermicity criterion). Adopting the procedure described above to generate an estimate for the enthalpy of formation of  $\text{SF}_2\text{Cl}^+$  yields  $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+) = 453 \text{ kJ mol}^{-1}$ . Even with the aid of this estimate it is not possible to identify conclusively the pathway that leads to the production of  $\text{SF}_2\text{Cl}^+$  from the reaction of  $\text{CO}_2^+$  with  $\text{SF}_5\text{Cl}$ , and two possible sets of neutral products are listed in Table 2. Dissociative charge transfer is not the route to  $\text{SF}_2\text{Cl}^+$ .  $\text{SF}_2\text{Cl}^+$  is also an observed product of the reaction with  $\text{H}_2\text{O}^+$ , and a chemical pathway such as:



is required to satisfy the exothermicity criterion. The reaction with  $\text{H}_2\text{O}^+$  also produces  $\text{SF}_2\text{OH}^+$ , providing direct confirmation that reactions involving the making as well as breaking of bonds do occur. An estimate for  $\Delta_f H_0^\circ(\text{SF}_2\text{OH}^+)$  can be obtained by assuming that  $D_0(\text{SF}_2^+-\text{OH}) \approx D_0(\text{SF}_2^+-\text{F})$ , which leads to  $\Delta_f H_0^\circ(\text{SF}_2\text{OH}^+) \approx 321 \text{ kJ mol}^{-1}$ . This is compatible with the formation of  $\text{SF}_2\text{OH}^+$  in the reaction of  $\text{H}_2\text{O}^+$  with  $\text{SF}_5\text{Cl}$ :



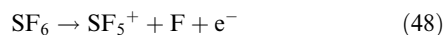
For the  $\text{CF}_m^+$  and  $\text{SF}_n^+$  reagent ions, which all have recombination energies less than 12.0 eV, *i.e.* well below the energy needed for dissociative ionisation of  $\text{SF}_5\text{Cl}$ , the majority of



**Fig. 5** A typical mass spectrum obtained from the chemical reaction of  $\text{CF}_3^+$  with  $\text{SF}_5\text{Cl}$ . Two product ions are observed;  $\text{SF}_5^+$  and  $\text{SF}_4\text{Cl}^+$ .



try has been constructed using enthalpies of formation for  $\text{CF}_m^+$ ,  $\text{CF}_m^{+24}$  and  $\text{SF}_n^+$ ,  $\text{SF}_n^{+25}$  from recent high level *ab initio* calculations. These *ab initio* values place the dissociative ionisation energy for:



at 14.18 eV. The dissociative ionisation limits of  $\text{SF}_6$  that lie below 22 eV are shown in Fig. 6. The high energies of the limits mean that only  $\text{Ne}^+$ ,  $\text{F}^+$ ,  $\text{Ar}^+$ ,  $\text{N}_2^+$ , and  $\text{N}^+$  may react with  $\text{SF}_6$  by dissociative charge transfer. All other reactions must occur by chemical pathways, for example:

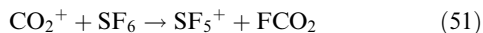


Williams *et al.*<sup>7</sup> have demonstrated that the reactions of  $\text{SF}_6$  with positive ions possessing recombination energies greater than 14.2 eV conform well to the expectations of models of long-range charge-transfer reactions. They also found evidence to indicate that the reaction of  $\text{SF}_6$  with  $\text{Ne}^+$  is mediated by short-range interactions. On thermochemical evidence they concluded that the minor  $\text{SF}_3^+$  product from the reaction of  $\text{N}^+$  with  $\text{SF}_6$  is the result of a chemical pathway leading to the formation of  $\text{NF}$  as one of the neutral products.

The slow reaction with  $\text{CO}_2^+$  is interesting. The obvious pathway to the observed  $\text{SF}_5^+$  product is dissociative charge transfer:



but this pathway is so endothermic ( $\Delta_r H_0^\circ(50) = 39 \text{ kJ mol}^{-1}$ ) that this reaction should not be observable with our SIFT apparatus at 300 K. It seems improbable that even a small fraction of the  $\text{CO}_2^+$  reagent ions possess sufficient internal energy to surmount the endothermicity. Instead, following the suggestion of Babcock and Streit,<sup>3</sup> the proposed pathway for the formation of  $\text{SF}_5^+$  is  $\text{F}^-$  transfer:



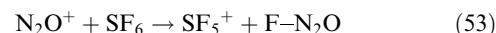
to form the weakly bound molecule  $\text{FCO}_2$ , providing a pathway to  $\text{SF}_5^+$  with a lower overall enthalpy change:

$$\Delta_r H_0^\circ(50) = \Delta_r H_0^\circ(49) - D_0(\text{F-CO}_2) \quad (52)$$

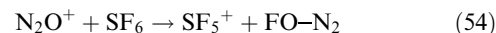
$\text{FC(O)O}$  has been characterised experimentally by a variety of spectroscopic methods.<sup>39,43,44</sup> The measurement of the electron affinity of  $\text{FCO}_2$  has led to the determination of  $D_0(\text{F-C(O)O}) = 48 \pm 13 \text{ kJ mol}^{-1}$ .<sup>39</sup> Theoretical calculations at the G2 level have given  $\Delta_r H_0^\circ(\text{FC(O)O}) = -378 \pm 8 \text{ kJ mol}^{-1}$ .<sup>40,41</sup> A very similar value ( $\Delta_r H_0^\circ(\text{FC(O)O}) = -376 \pm 13 \text{ kJ mol}^{-1}$ ) has resulted from the use of density functional theory to calculate the enthalpy changes for a number of isodesmic reactions involving  $\text{FC(O)O}$ .<sup>42</sup> Combining these theoretical values with  $\Delta_r H_0^\circ(\text{CO}_2)$  and  $\Delta_r H_0^\circ(\text{F})$  from the JANAF tables<sup>27</sup> gives  $D_0(\text{F-C(O)O}) = 61 \pm 15 \text{ kJ mol}^{-1}$ . Either value for  $D_0(\text{F-C(O)O})$  leads to the conclusion that reaction (51) is exothermic. The observed low rate coefficient for the reaction of  $\text{CO}_2^+$  with  $\text{SF}_6$  ( $k_{\text{exp}}/k_c = 0.008$ ) may reflect a barrier associated with  $\text{F}^-$  abstraction from  $\text{SF}_6$ , which is not fully removed by the small overall exothermicity of the reaction. Several other reactions in which  $\text{F}^-$  is abstracted from  $\text{SF}_6$  also have rate constants less than predicted by capture theory (see below).

The slow reaction of  $\text{N}_2\text{O}^+$  with  $\text{SF}_6$  to form  $\text{SF}_5^+$  provides another example of a reaction where it is necessary to postulate the formation of a weakly bound product in order to provide a pathway with a sufficiently low overall endothermicity to be

consistent with an observable rate coefficient. Two possibilities are:



and



with 0 K enthalpy changes given by:

$$[\Delta_r H_0^\circ(52)/\text{kJ mol}^{-1}] = 124 - [D_0(\text{F-N}_2\text{O})/\text{kJ mol}^{-1}] \quad (55)$$

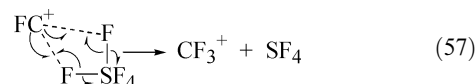
and

$$[\Delta_r H_0^\circ(53)/\text{kJ mol}^{-1}] = 69 - [D_0(\text{FO-N}_2)/\text{kJ mol}^{-1}] \quad (56)$$

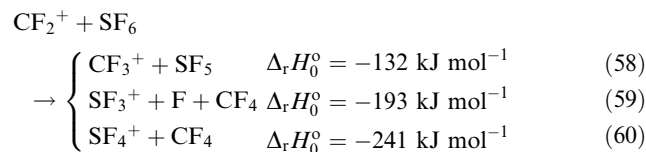
There appears to be no independent evidence for the existence of any isomer of  $\text{FN}_2\text{O}$ , and  $D_0(\text{F-N}_2\text{O})$  and  $D_0(\text{FO-N}_2)$  are unknown.

$\text{F}^-$  abstraction from  $\text{SF}_6$  to form  $\text{SF}_5^+$  is exothermic for  $\text{CF}^+$ ,  $\text{CF}_2^+$ , and  $\text{CF}_3^+$ , but for each of these reactions the experimental rate coefficient ( $k_{\text{exp}}$ ) is less than the calculated value from Langevin capture theory ( $k_c$ ), and for  $\text{CF}_3^+$   $k_{\text{exp}} \approx 0.25 \times k_c$ . The efficiencies of the reactions, defined as  $k_{\text{exp}}/k_c$ , are plotted in Fig. 2 against the fluoride affinities of the reagent ions, to show the correlation between reaction efficiency and reagent ion fluoride affinity.

A minor product from the reaction of  $\text{CF}^+$  is  $\text{CF}_3^+$ . Sequential transfer of two F atoms is unlikely to be the mechanism for the first step (to form  $\text{CF}_2^+ + \text{SF}_5$ ) is highly endothermic ( $\Delta_r H_0^\circ = 156 \text{ kJ mol}^{-1}$ ). Instead the transfer must be concerted:

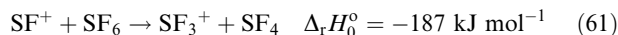


The greater complexity of this scheme, compared to the much less exothermic  $\text{F}^-$  abstraction leading to  $\text{SF}_5^+$ , provides an explanation for the higher branching ratio to form  $\text{SF}_5^+$  compared to  $\text{CF}_3^+$ . With  $\text{CF}_2^+$  as the reagent ion, there are several pathways of greater exothermicity than  $\text{F}^-$  abstraction:

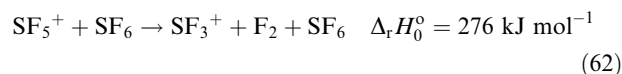


yet the ion products of these reactions were not observed.

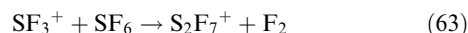
For the  $\text{SF}_n^+$  reagent ions, only one exothermic pathway was identified:



but this reaction, involving the transfer of two F atoms, was not observed. In experiments using non-thermal reagent ions,<sup>5,45</sup> evidence has been presented for the occurrence of the endothermic reaction:



and for:

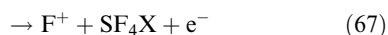
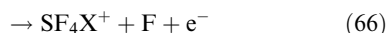
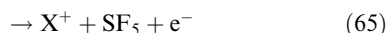
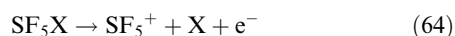


The reaction products are only accessible for reagent ions which are translationally and/or internally excited, and the reactions are not observed in SIFT experiments, where the ions have been thermalised before they can react.

F<sup>−</sup> abstraction is calculated to be highly endothermic for NO<sup>+</sup> and NO<sub>2</sub><sup>+</sup>, and SF<sub>6</sub> does not react with either of these reagent ions. SF<sub>6</sub> has a much lower proton affinity than H<sub>2</sub>O,<sup>46</sup> and as a consequence there is no reaction between H<sub>3</sub>O<sup>+</sup> and SF<sub>6</sub>.

### 3.4 Comparisons

The parent cation SF<sub>5</sub>X<sup>+</sup> (X = CF<sub>3</sub>, Cl, F) was not observed as a product from any of the reactions. When it is formed by charge transfer, it immediately dissociates. The most obvious pathways for dissociative ionisation involve scission of one bond:

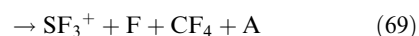
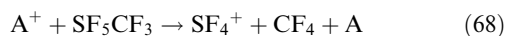


with smaller SF<sub>p</sub><sup>+</sup> (*p* < 5) and SF<sub>q</sub>X<sup>+</sup> (*q* < 4) ions resulting from stepwise fragmentation of SF<sub>5</sub><sup>+</sup> and SF<sub>4</sub>X<sup>+</sup>. F<sup>+</sup> was not observed among the ion products for any of the reactions. Even with Ne<sup>+</sup>, the reagent ion with the highest recombination energy, the products of pathway (67) are energetically inaccessible for SF<sub>6</sub>, and barely accessible for SF<sub>5</sub>CF<sub>3</sub> and SF<sub>5</sub>Cl. Dissociative channels (64) and (65) differ only in the location of the positive charge. For X = Cl and F, channel (65) lies higher in energy than (64), by 3.42 eV (330 kJ mol<sup>−1</sup>) for X = Cl, and by 7.88 eV (760 kJ mol<sup>−1</sup>) for X = F, but for X = CF<sub>3</sub> channel (65) is below (64) by 0.50 eV (48 kJ mol<sup>−1</sup>). For channel (64) the S–X bond is broken, channel (66) corresponds to breaking an S–F bond. The energy differences between (64) and (66) can be obtained using our estimates of Δ<sub>F</sub>H<sub>0</sub><sup>0</sup>(SF<sub>4</sub>CF<sub>3</sub><sup>+</sup>) (= −221 to −348 kJ mol<sup>−1</sup>) and Δ<sub>F</sub>H<sub>0</sub><sup>0</sup>(SF<sub>4</sub>Cl<sup>+</sup>) (~150 kJ mol<sup>−1</sup>). For SF<sub>5</sub>CF<sub>3</sub> the products of (60) lie considerably below those of (66), the difference is between 1.13 and 2.45 eV (109 and 236 kJ mol<sup>−1</sup>). In the case of SF<sub>5</sub>Cl, the difference between (64) and (66) is small, 0.24 eV (23 kJ mol<sup>−1</sup>), with (66) being the lower energy channel.

These energy differences play a significant role in determining the products observed from the charge-transfer reactions of the SF<sub>5</sub>X molecules. In the case of SF<sub>5</sub>CF<sub>3</sub>, for reagent ions with recombination energies in excess of 12.9 eV, the experimentally determined limit for (65),<sup>10</sup> CF<sub>3</sub><sup>+</sup> is the dominant product ion. The ratio of SF<sub>5</sub><sup>+</sup> to CF<sub>3</sub><sup>+</sup> increases with the recombination energy of the reagent ion, reflecting the higher energy of (64) compared to (65). The energy difference between (66) and (65) is quite large, and SF<sub>4</sub>CF<sub>3</sub><sup>+</sup> was observed as a trace product from only a few of the reactions. The pattern of the energies of the channels is quite different for SF<sub>5</sub>Cl (compare Figs. 1 and 3), (64) is the lowest (12.32 eV<sup>30,36</sup>), (66) is only slightly higher (12.56 eV), with (65) much higher (15.74 eV). The relative branching ratios for SF<sub>5</sub><sup>+</sup> and SF<sub>4</sub>Cl<sup>+</sup> vary greatly, and there is no obvious correlation with the recombination energy of the reagent ion. The TPEPICO experiments on the fragmentation of energy-selected SF<sub>5</sub>Cl<sup>+</sup> ions<sup>36</sup> do not show these variations. The results thus show a deviation from the predictions of long-range charge-transfer theory. This suggests that when the energy difference between two channels is small, short-range interactions within the ion-molecule complex between formation by capture and break-up leading to the release of the products can have a large effect on the relative yields of different product ions. For SF<sub>6</sub> the only energetically accessible channel is (64), which is identical to (66). Available energy appears to be the most important factor in determining the outcome of the charge-transfer reactions.

Various SF<sub>p</sub><sup>+</sup> (*p* < 5) and SF<sub>q</sub>X<sup>+</sup> (*q* < 4) ions were observed from the charge-transfer reactions. In many cases these can be formed by fragmentation of SF<sub>5</sub><sup>+</sup> and SF<sub>4</sub>X<sup>+</sup>. However, con-

sideration of the energetics indicates that in some cases the appearance of certain fragment ions is only possible if new bonds are formed. The great majority of these cases occur for SF<sub>5</sub>CF<sub>3</sub>, where exothermic charge-transfer routes to SF<sub>3</sub><sup>+</sup> and SF<sub>4</sub><sup>+</sup> in general require the formation of CF<sub>4</sub> as one of the neutral products:



Reactions of this type can be identified in Table 1. The high bond dissociation energy *D*<sub>0</sub>(CF<sub>3</sub>–F) (= 374 kJ mol<sup>−1</sup>) is a strong thermochemical driving force for these reactions of SF<sub>5</sub>CF<sub>3</sub>. For SF<sub>5</sub>Cl and SF<sub>6</sub>, the fragment ions SF<sub>4</sub><sup>+</sup> and SF<sub>3</sub><sup>+</sup> are not observed at energies well below the limits for their formation by stepwise loss of atoms from SF<sub>5</sub>Cl<sup>+</sup> and SF<sub>6</sub><sup>+</sup> (reaction scheme (33)). *D*<sub>0</sub>(Cl–F) (= 247 kJ mol<sup>−1</sup>) and *D*<sub>0</sub>(F–F) (= 154 kJ mol<sup>−1</sup>) are much lower than *D*<sub>0</sub>(CF<sub>3</sub>–F), and there are few examples of reactions requiring the formation of ClF or F<sub>2</sub>. In addition, the XF forming pathways to SF<sub>4</sub><sup>+</sup> and SF<sub>3</sub><sup>+</sup> can be viewed as dissociation of SF<sub>5</sub>X<sup>+</sup> (→SF<sub>5</sub> + X<sup>+</sup>) coupled with abstraction of F<sup>−</sup> from SF<sub>5</sub> by X<sup>+</sup>. This will be a much higher energy pathway for SF<sub>5</sub>Cl and SF<sub>6</sub> than for SF<sub>5</sub>CF<sub>3</sub>, because of the higher ionisation energy of Cl (12.97 eV) and F (17.42 eV) compared to CF<sub>3</sub> (9.04 eV). The formation of SF<sub>3</sub><sup>+</sup> from the reactions of N<sup>+</sup>, CO<sub>2</sub><sup>+</sup>, and H<sub>2</sub>O<sup>+</sup> with SF<sub>5</sub>Cl probably involves the formation of ClF or ClF<sub>2</sub>. In the case of SF<sub>6</sub>, the formation of SF<sub>3</sub><sup>+</sup> from the reaction with F<sup>+</sup> requires the formation of F<sub>2</sub>. Other charge-transfer reactions of each of the molecules may occur with the formation of new bonds, but without identification of the neutral products this cannot be demonstrated.

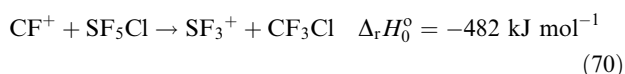
Almost all of the (presumed) charge-transfer reactions proceed with rate constants close to the values calculated by capture theories. The only clear exception is the reaction of Ne<sup>+</sup> with SF<sub>6</sub>. According to the long-range charge-transfer model *k*<sub>exp</sub> ≈ *k*<sub>c</sub> implies that there is a match between the recombination energy of the reagent ion (RE) and a band in the photoelectron spectrum of the molecule. A photoelectron spectrum is not available for SF<sub>5</sub>CF<sub>3</sub>. For SF<sub>5</sub>Cl there is a good match between a band in the photoelectron spectrum<sup>29</sup> and the recombination energy of each of the reagent ions, including Ne<sup>+</sup>, for which charge-transfer reactions are energetically possible (*i.e.* RE > 12.3 eV). In the case of SF<sub>6</sub>, the match for Ne<sup>+</sup> is poor, which provides an explanation for the low rate coefficient for the reaction, compared to the capture theory prediction.<sup>7</sup>

Since the product neutrals from the reactions cannot be detected, the identification of charge-transfer reactions is based on a combination of knowledge of the product ions and basic energetic data. Without energetic data on the dissociative ionisation limits of the molecules, obtained from various photoionisation experiments<sup>10,30,36</sup> and theoretical calculations,<sup>24,25</sup> it would be impossible to discern when the reaction mechanism must change from charge transfer to a chemical pathway.

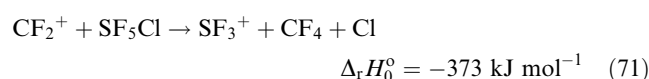
The reagent ions CF<sub>*m*</sub><sup>+</sup> (*m* = 1–3) and SF<sub>*n*</sub><sup>+</sup> (*n* = 1–5) all have recombination energies below 12.0 eV, so their reactions with SF<sub>5</sub>CF<sub>3</sub>, SF<sub>5</sub>Cl, and SF<sub>6</sub> must occur *via* chemical pathways. The observed ion products of the reactions of these ions with SF<sub>5</sub>CF<sub>3</sub> (mainly SF<sub>3</sub><sup>+</sup> and CF<sub>3</sub><sup>+</sup>) show that they are mechanistically quite different from their reactions with SF<sub>5</sub>Cl (SF<sub>4</sub>Cl<sup>+</sup> and SF<sub>5</sub><sup>+</sup> are the major products) and SF<sub>6</sub> (primarily yield SF<sub>5</sub><sup>+</sup>). While the major reaction pathways for SF<sub>5</sub>Cl and SF<sub>6</sub> are simple Cl<sup>−</sup> and F<sup>−</sup> abstractions, for SF<sub>5</sub>CF<sub>3</sub> transfer of F<sup>−</sup> to the reagent ion is combined with breaking the S–C bond (see reaction schemes (18) and (19)). In large part the differences between SF<sub>5</sub>CF<sub>3</sub> and the other two reactants appear to follow the thermochemistry of the reaction pathways.

Mechanism (18) is the proposed pathway to SF<sub>3</sub><sup>+</sup>, which is an observed product from the reactions of SF<sub>5</sub>CF<sub>3</sub> with each of the CF<sub>*m*</sub><sup>+</sup> and SF<sub>*n*</sub><sup>+</sup> reagent ions, except SF<sub>3</sub><sup>+</sup> and SF<sub>2</sub><sup>+</sup>. For SF<sub>3</sub><sup>+</sup>

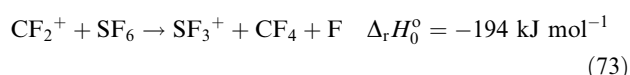
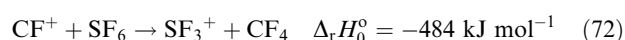
it is not possible to distinguish product  $\text{SF}_3^+$  from the reagent ions. For  $\text{SF}_2^+$ , the calculated enthalpy change for the production of  $\text{SF}_3^+$  ( $\Delta_r H_0^\circ = -21 \text{ kJ mol}^{-1}$ ) reveals that pathway (18) is less exothermic than for the reactions of other reagent ions with  $\text{SF}_5\text{CF}_3$  in which  $\text{SF}_3^+$  is an observed product (see Table 1). This must be an important factor in making the reaction of  $\text{SF}_2^+$  too slow to be detected. As the group X of  $\text{SF}_5\text{X}$  changes from  $\text{CF}_3$  to Cl and then F pathway (18) becomes increasingly less exothermic, due mainly to the decreasing strength of the new X–F bond. In the case of  $\text{SF}_5\text{Cl}$ , pathway (18) is only calculated to be exothermic for the  $\text{CF}_m^+$  reagent ions. The  $\text{SF}_3^+$  product ion was only observed from the reaction of  $\text{CF}^+$ . With  $\text{CF}^+$  as the reagent ion, the calculated exothermicity ( $-23 \text{ kJ mol}^{-1}$ ) is less than for  $\text{CF}_3^+$  ( $-41 \text{ kJ mol}^{-1}$ ) and  $\text{CF}_2^+$  ( $-80 \text{ kJ mol}^{-1}$ ) which suggests that the  $\text{CF}^+$  reaction may proceed by a different, more exothermic pathway:



There is a highly exothermic pathway to  $\text{SF}_3^+$  for  $\text{CF}_2^+$ :



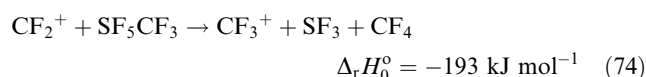
but  $\text{SF}_3^+$  was not one of the detected ion products from the reaction of  $\text{CF}_2^+$  with  $\text{SF}_5\text{Cl}$ . For  $\text{SF}_6$ , pathway (18) to  $\text{SF}_3^+$  is in every case endothermic. There are exothermic pathways, analogous to (70) and (71) above, when the reagent ion is  $\text{CF}^+$  and  $\text{CF}_2^+$ :



but  $\text{SF}_3^+$  was not one of the detected product ions from the reactions of  $\text{CF}^+$  and  $\text{CF}_2^+$  with  $\text{SF}_6$ . Exothermicity alone is not sufficient to predict the outcome of these ‘chemical’ ion-molecule reactions.

Most of the reactions of  $\text{SF}_5\text{CF}_3$  lead to the formation of  $\text{CF}_3^+$  as one of the ion products. Reaction scheme (19) is the most likely pathway. Whenever (19) is exothermic or close to thermoneutral,  $\text{CF}_3^+$  is detected.  $\text{Cl}^+$  and  $\text{F}^+$  were not observed from the reactions of  $\text{SF}_5\text{Cl}$  and  $\text{SF}_6$  with  $\text{CF}_m^+$  and  $\text{SF}_n^+$ . This is due to the high ionisation energies of Cl and F, compared to  $\text{CF}_3$ , making all pathways to  $\text{Cl}^+$  and  $\text{F}^+$  endothermic.

The transfer of  $\text{F}^-$  to the reagent ion to form  $\text{SF}_4\text{X}^+$  was observed whenever this pathway is exothermic. The occurrence of this reaction for particular reagent ion/neutral reactant combinations then depends on the difference between the fluoride affinity of the reagent ion and of  $\text{SF}_4\text{X}^+$ . Using our bounds for  $\Delta_r H_0^\circ(\text{SF}_4\text{CF}_3^+)$ , the fluoride affinity of  $\text{SF}_4\text{CF}_3^+$  lies between 1074 and 1201  $\text{kJ mol}^{-1}$ , which is greater than for  $\text{SF}_5^+$  (1040  $\text{kJ mol}^{-1}$ ) and  $\text{SF}_4\text{Cl}^+$  (884  $\text{kJ mol}^{-1}$ ). This is reflected in the observation that the ion product of  $\text{F}^-$  transfer is seen for many of the reactions of  $\text{SF}_5\text{Cl}$ , and for the reactions of  $\text{SF}_6$  with each of the  $\text{CF}_n^+$  reagent ions. In contrast,  $\text{SF}_4\text{CF}_3^+$  was seen only as a trace product from the reaction of  $\text{SF}_5\text{CF}_3$  with  $\text{CF}_2^+$ . F atom transfer may occur in the reaction of  $\text{CF}_2^+$  with  $\text{SF}_5\text{CF}_3$ , but the observed  $\text{CF}_3^+$  product may result from a number of other pathways, including (19) and:



For  $\text{SF}_5\text{CF}_3$  and  $\text{SF}_5\text{Cl}$  there is the possibility of transferring  $\text{CF}_3^-$  ( $\text{Cl}^-$ ) and  $\text{CF}_3$  (Cl) in addition to  $\text{F}^-$  and F. Compared

to the other  $\text{CF}_m^+$  and  $\text{SF}_n^+$  reagent ions,  $\text{CF}_2^+$  is expected to have the highest affinity for  $\text{CF}_3$  and Cl. The only example of transfer of a Cl atom is the reaction of  $\text{CF}_2^+$  with  $\text{SF}_5\text{Cl}$ , where it is highly exothermic (see Table 2). The reaction is facilitated by the relatively low  $\text{SF}_5\text{--Cl}$  bond strength ( $D_0(\text{SF}_5\text{--Cl}) = 268 \text{ kJ mol}^{-1}$ , compared to  $D_0(\text{SF}_5\text{--CF}_3) = 374 \text{ kJ mol}^{-1}$ , and  $D_0(\text{SF}_5\text{--F}) = 447 \text{ kJ mol}^{-1}$ ). Using  $\Delta_r H_0^\circ(\text{CF}_3\text{CF}_2^+) = 14 \text{ kJ mol}^{-1}$ ,<sup>47</sup> the transfer of  $\text{CF}_3$  from  $\text{SF}_5\text{CF}_3$  to  $\text{CF}_2^+$  is calculated to be exothermic ( $\Delta_r H_0^\circ = -60 \text{ kJ mol}^{-1}$ ), but  $\text{CF}_3\text{CF}_2^+$  was not observed. Transfer of  $\text{CF}_3^-$  ( $\text{Cl}^-$ ) leads to the formation of  $\text{SF}_5^+$ .  $\text{SF}_5^+$  was detected as an ion product from a number of reactions, and in each case the  $\text{CF}_3^-$  ( $\text{Cl}^-$ ) transfer pathway is calculated to be exothermic (for  $\text{CF}^+$  reacting with  $\text{SF}_5\text{CF}_3$  a rearrangement of the neutral product is required).

The only reactions which do not fall into the above categories are those of  $\text{CF}^+$  with  $\text{SF}_5\text{Cl}$  ( $\rightarrow \text{CF}_2\text{Cl}^+$ ), and  $\text{SF}_6$  ( $\rightarrow \text{CF}_3^+$ ). For  $\text{SF}_5\text{CF}_3$ , the  $\text{CF}_3^+$  product can result from reaction scheme (19), but a very different mechanism must operate for  $\text{SF}_5\text{Cl}$  and  $\text{SF}_6$ . An exothermic route to  $\text{CF}_2\text{Cl}^+$  and  $\text{CF}_3^+$ , respectively, is obtained by transferring Cl + F and F + F, respectively, (mechanism (46) for  $\text{SF}_5\text{Cl}$ , and (57) for  $\text{SF}_6$ ) to the reagent  $\text{CF}^+$ . This mechanism might also be operative for  $\text{SF}_5\text{CF}_3$ , in which case the neutral product would be  $\text{SF}_3\text{--CF}_3$ . The suggestion that the production of  $\text{CF}_3^+$  from  $\text{SF}_5\text{CF}_3$  occurs by a different mechanism from the formation of  $\text{CF}_2\text{Cl}^+$  from  $\text{SF}_5\text{Cl}$ , and  $\text{CF}_3^+$  from  $\text{SF}_6$ , is supported by the very different product ion yields (47%  $\text{CF}_3^+$  ( $\text{SF}_5\text{CF}_3$ ), 3%  $\text{CF}_2\text{Cl}^+$  ( $\text{SF}_5\text{Cl}$ ), and 5%  $\text{CF}_3^+$  ( $\text{SF}_6$ )).

The major ion products of the reactions with  $\text{CF}_m^+$  and  $\text{SF}_n^+$  are formed through mechanisms that commence with the abstraction of  $\text{F}^-$  ( $\text{Cl}^-$  in the case of the reactions of  $\text{SF}_5\text{Cl}$  which form  $\text{SF}_5^+$ ). Fig. 2 shows how the efficiencies of the reactions vary with the  $\text{F}^-$  affinity of the reagent ion. In addition to the anticipated general increase in overall efficiency with  $\text{F}^-$  affinity, it is observed that for each of the reagent ions the efficiencies are in the sequence  $\text{SF}_5\text{Cl} > \text{SF}_5\text{CF}_3 > \text{SF}_6$ . This does not follow the order of the energies needed for  $\text{F}^-$  abstraction from the molecules ( $\text{SF}_5\text{Cl} < \text{SF}_6 < \text{SF}_5\text{CF}_3$ ), which provides further evidence of mechanistic differences for the reactions of  $\text{SF}_5\text{CF}_3$  compared to those of  $\text{SF}_5\text{Cl}$  and  $\text{SF}_6$ . The reaction of  $\text{SF}^+$  with  $\text{SF}_5\text{Cl}$  has an unexpectedly high efficiency (0.67 for  $\text{SF}_5\text{Cl}$ , compared to 0.025 for  $\text{SF}_5\text{CF}_3$ ). As discussed earlier, on the basis of the observed ion products, this reaction proceeds primarily by  $\text{Cl}^-$  rather than  $\text{F}^-$  abstraction. The trends between  $\text{CF}^+$ ,  $\text{CF}_2^+$ , and  $\text{CF}_3^+$  are the same for each of the reactant molecules, with  $\text{CF}_3^+$  in each case having a significantly lower reaction efficiency than both  $\text{CF}^+$  and  $\text{CF}_2^+$ , even though the  $\text{F}^-$  affinity of  $\text{CF}_3^+$  is greater than that of  $\text{CF}^+$ . This is suggestive of some steric factor impeding the reaction of the relatively bulky  $\text{CF}_3^+$  to a greater extent than for  $\text{CF}^+$  and  $\text{CF}_2^+$ .

## 4. Conclusions

Rate coefficients and product ion distributions are reported for the reactions of twenty-two atomic and molecular reagent cations with two derivatives of  $\text{SF}_6$ ;  $\text{SF}_5\text{CF}_3$  and  $\text{SF}_5\text{Cl}$ . The reagent ions have a wide range of recombination energies, so that both charge transfer and chemical ion-molecule reactions are observed. Most of the reactions proceed with rate coefficients close to the predictions of capture theories. There are notable exceptions to this, as can be seen by inspecting the data in Tables 1 to 3. A variety of reaction processes are evident, including dissociative charge transfer and various abstraction routes.  $\text{SF}_5\text{X}^+$  ( $\text{X} = \text{F}, \text{Cl}, \text{CF}_3$ ) ions were not observed as products of any of the reactions. Although there may well be bound regions on the potential energy surfaces of the parent ions, these are not accessed in charge-transfer reactions. Instead, as seen in studies of the photoionisation of  $\text{SF}_5\text{X}$ ,



the initially formed  $\text{SF}_5\text{X}^+$  ions dissociate very rapidly over repulsive energy surfaces.

The observed ion products show that the reactions of  $\text{SF}_5\text{CF}_3$  are quite different from those of  $\text{SF}_5\text{Cl}$  and  $\text{SF}_6$ . The major products from the charge-transfer reactions of reagent ions  $\text{A}^+$  with  $\text{SF}_5\text{CF}_3$  are  $\text{SF}_3^+$  ( $+\text{CF}_4 + \text{F} + \text{A}$ ) and  $\text{CF}_3^+$  ( $+\text{SF}_5 + \text{A}$ ), while  $\text{SF}_5^+$  ( $+\text{Cl} + \text{A}$ ) and  $\text{SF}_4\text{Cl}^+$  ( $+\text{F} + \text{A}$ ) are formed from  $\text{SF}_5\text{Cl}$ , and  $\text{SF}_5^+$  ( $+\text{F} + \text{A}$ ) from  $\text{SF}_6$ . These differences can be traced to the thermochemistry of the reactions, the energies of the dissociative ionisation pathways are shown in Figs. 1, 3, and 6. The high dissociation energy of  $\text{CF}_3\text{--F}$  ( $374 \text{ kJ mol}^{-1}$ ) compared to  $\text{F--Cl}$  ( $247 \text{ kJ mol}^{-1}$ ) and  $\text{F--F}$  ( $154 \text{ kJ mol}^{-1}$ ) accounts for the appearance of  $\text{SF}_3^+$  from  $\text{SF}_5\text{CF}_3$ . The low ionisation energy of  $\text{CF}_3$  ( $9.04 \text{ eV}$ ) compared to  $\text{SF}_5$  ( $9.52 \text{ eV}$ ),  $\text{Cl}$  ( $12.97 \text{ eV}$ ), and  $\text{F}$  ( $17.42 \text{ eV}$ ) is responsible for the formation of  $\text{CF}_3^+$  and little  $\text{SF}_5^+$  from  $\text{SF}_5\text{CF}_3$ , while the ion products from  $\text{SF}_5\text{Cl}$  are  $\text{SF}_5^+$  and  $\text{SF}_4\text{Cl}^+$ , and  $\text{SF}_5^+$  from  $\text{SF}_6$ . These energetic factors also influence the products of chemical ion-molecule reactions of the molecules. Thus the major ion products from  $\text{SF}_5\text{CF}_3$  are again  $\text{SF}_3^+$  and  $\text{CF}_3^+$ ,  $\text{SF}_5\text{Cl}$  produces mainly  $\text{SF}_5^+$  and  $\text{SF}_4\text{Cl}^+$ , and  $\text{SF}_6$  yields  $\text{SF}_5^+$ .

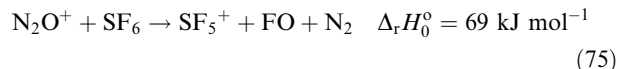
The charge-transfer reactions generally conform well to the expectations of models of long-range charge-transfer processes. However, it was noted that some of the reactions of  $\text{SF}_5\text{CF}_3$ , specifically those with  $\text{N}^+$ ,  $\text{CO}^+$ ,  $\text{CO}_2^+$ ,  $\text{O}^+$ , and  $\text{N}_2\text{O}^+$ , produced more  $\text{SF}_3^+$  than expected on the basis of TPEPICO experiments on the fragmentation of isolated energy selected ( $\text{SF}_5\text{CF}_3^+$ )\*. Also the wide variations in the  $\text{SF}_4\text{Cl}^+/\text{SF}_5^+$  ratio with the recombination energy of the reagent ion are not compatible with other data on the ionisation of  $\text{SF}_5\text{Cl}$ . There is thus evidence that short-range interactions can influence the outcome of fast charge-transfer reactions.

$\text{F}^-$  abstraction and processes in which  $\text{F}^-$  abstraction is coupled to other chemical transformations dominate the reactions of ions such as  $\text{CF}_m^+$  and  $\text{SF}_n^+$ , which have recombination energies below the lowest dissociative ionisation limits of  $\text{SF}_5\text{CF}_3$ ,  $\text{SF}_5\text{Cl}$ , and  $\text{SF}_6$ . Many of these reactions have rate coefficients below those predicted by capture theories, the efficiencies generally do correlate with the fluoride affinity of the reagent ion. Lower than expected efficiencies for the reactions of  $\text{CF}_3^+$ , when compared against  $\text{CF}^+$  and  $\text{CF}_2^+$ , may be indicative of steric factors associated with the relatively bulky  $\text{CF}_3^+$  reagent ion. As for the charge-transfer reactions, the ion products show that  $\text{SF}_5\text{CF}_3$  reacts by pathways that are mechanistically distinct from the routes followed by  $\text{SF}_5\text{Cl}$  and  $\text{SF}_6$ . For  $\text{SF}_5\text{CF}_3$  the major products from the chemical reaction with  $\text{A}^+$  are  $\text{CF}_3^+$  ( $+\text{SF}_4 + \text{AF}$ ) and  $\text{SF}_3^+$  ( $+\text{CF}_4 + \text{AF}$ ),  $\text{SF}_5\text{Cl}$  forms  $\text{SF}_5^+$  ( $+\text{Cl}$ ) and  $\text{SF}_4\text{Cl}^+$  ( $+\text{F}$ ), and  $\text{SF}_6$  yields  $\text{SF}_5^+$  ( $+\text{F}$ ). These differences are again attributed to the energetics - the low ionisation potential of  $\text{CF}_3$ , and the high  $\text{CF}_3\text{--F}$  bond dissociation energy are major factors.

We have chosen to base our thermochemical analysis of the reactions on enthalpies of formation for  $\text{CF}_m^+$  and  $\text{SF}_n^+$  taken from recent *ab initio* calculations.<sup>24,25</sup> This immediately impacts on the enthalpies of formation of  $\text{SF}_5\text{CF}_3$  and  $\text{SF}_5\text{Cl}$ , which can be derived from appearance energies of  $\text{SF}_5 + \text{CF}_3^+$  and  $\text{SF}_5^+ + \text{Cl}$ , respectively, obtained from photoionisation experiments.<sup>10,30</sup> We have adopted  $\Delta_f H_0^\circ(\text{SF}_5\text{CF}_3) = -1673 \text{ kJ mol}^{-1}$  and  $\Delta_f H_0^\circ(\text{SF}_5\text{Cl}) \geq -985 \text{ kJ mol}^{-1}$ .

Central to our analysis of the results is the exothermicity criterion, that for a particular ion product to be observed in a SIFT study of a reaction, there must be a pathway that is exothermic, or at least close to thermoneutral. Use of this criterion has allowed us to propose values for the enthalpies of formation of some of the product ions, these include:  $-348 \text{ kJ mol}^{-1} < \Delta_f H_0^\circ(\text{SF}_4\text{CF}_3^+) < -221 \text{ kJ mol}^{-1}$ , and  $\Delta_f H_0^\circ(\text{SF}_4\text{Cl}^+) = 150 \text{ kJ mol}^{-1}$ . Values for a number of  $\text{SF}_p\text{Cl}^+$  ions were suggested by comparisons with  $\text{SF}_{p+1}^+$  ions,

and shown to be consistent with the observation of  $\text{SF}_p\text{Cl}^+$  from some of the reactions of  $\text{SF}_5\text{Cl}$ . These include:  $\Delta_f H_0^\circ(\text{SFCl}^+) = 782 \text{ kJ mol}^{-1}$ , and  $\Delta_f H_0^\circ(\text{SF}_2\text{Cl}^+) = 453 \text{ kJ mol}^{-1}$ . Other estimated values are  $\Delta_f H_0^\circ(\text{SF}_2\text{OH}^+) = 321 \text{ kJ mol}^{-1}$ , and  $\Delta_f H_0^\circ(\text{SF}_4\text{Cl}) = -761 \text{ kJ mol}^{-1}$ . With one exception there are no observed reactions for which, allowing for uncertainties in the values of the enthalpies of formation, the enthalpy of reaction is greater than  $+20 \text{ kJ mol}^{-1}$ . The one exception is the slow reaction between  $\text{N}_2\text{O}^+$  and  $\text{SF}_6$ , to form  $\text{SF}_5^+$ . The least endothermic pathway to  $\text{SF}_5^+$  is:



but, as calculated, this is too endothermic to account for the formation of  $\text{SF}_5^+$ . It is unlikely that the weak binding between  $\text{FO--N}_2$  can be sufficiently strong to make the reactions proceed with a high enough rate coefficient to be observable by the SIFT technique at 300 K. Thus the observation of  $\text{SF}_5^+$  from the reaction of  $\text{SF}_6$  with  $\text{N}_2\text{O}^+$  suggests that  $\Delta_f H_0^\circ(\text{SF}_5^+) = 84 \text{ kJ mol}^{-125}$  is too high. The experimental data on  $\text{SF}_5\text{Cl}$  may also point to a problem with  $\Delta_f H_0^\circ(\text{SF}_5^+)$ . If the observed appearance energy of  $12.32 \text{ eV}$  for the dissociative photoionisation (28)<sup>30</sup> is combined with  $\Delta_f H_0^\circ(\text{SF}_5\text{Cl}) = -1026 \text{ kJ mol}^{-1,27}$  obtained from calorimetric measurements,<sup>28</sup> then  $\Delta_f H_0^\circ(\text{SF}_5^+) \leq 43 \text{ kJ mol}^{-1}$ . Chim *et al.*<sup>10</sup> have sought to determine the dissociative ionisation energy of  $\text{SF}_6$  ( $\rightarrow \text{SF}_5^+ + \text{F} + \text{e}^-$ ) by extrapolation of TPEPICO data to zero kinetic energy release. From a rather long extrapolation they determined the dissociative ionisation energy to be  $13.6 (\pm 0.1) \text{ eV}$ , when combined with standard literature values for  $\Delta_f H_0^\circ(\text{SF}_6)$  and  $\Delta_f H_0^\circ(\text{F})$ <sup>27</sup> this result gives  $\Delta_f H_0^\circ(\text{SF}_5^+) = 28 \text{ kJ mol}^{-1}$ .  $\Delta_f H_0^\circ(\text{SF}_5^+) = 84 \text{ kJ mol}^{-125}$  is strongly supported by other theoretical calculations.<sup>48,49</sup> Irikura<sup>50</sup> has proposed that  $\Delta G^\circ (= \Delta H^\circ - T\Delta S^\circ)$  rather than  $\Delta H_0^\circ$  might be used to predict the spontaneity (observation) of gas-phase ion-molecule reactions. This introduces entropic factors, which we have ignored in our analysis of the thermodynamics of the reactions. For reactions in which there is an increase in the number of molecules (*e.g.* (75)),  $\Delta S^\circ > 0$ , making  $\Delta G^\circ < \Delta H^\circ$ , so that if  $\Delta G^\circ < 0$  is the criterion, then endothermic reactions may become observable. For the two reactions  $\Delta S_{298}^\circ(75) = 180.76 \text{ J K}^{-1} \text{ mol}^{-1,27}$  neglecting the small temperature dependence of  $\Delta H^\circ$ ,  $\Delta G_{298}^\circ(75) = 15 \text{ kJ mol}^{-1}$ , suggesting that  $\text{SF}_5^+$  might be produced by reaction (75), and that the reaction would have a low efficiency. However, for reactions in which there is a change in the number of molecules, both  $\Delta S$  and  $\Delta G$  change with the partial pressures of the reactants and products. It is then not clear that  $\Delta G_{298}^\circ$  will be the correct quantity from which to predict whether a particular ion-molecule reaction will be observable using the SIFT technique.

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