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*J. Phys. Chem. A.*, (2000) **104**, 10766-10776

DOI: 10.1021/jp002120z

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Professor Richard Tuckett (University of Birmingham) / July 2011

*Version2 submitted 29.8.2000*

**A Selected Ion Flow Tube Study of the Reactions of Several Cations with the Group 6B  
Hexafluorides, SF<sub>6</sub>, SeF<sub>6</sub> and TeF<sub>6</sub>**

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Submitted : May 2000 to J. Phys. Chem. A, revised version 29.8.2000

Reference number : JP002120Z

## Abstract

The first investigation of the ion chemistry of  $\text{SeF}_6$  and  $\text{TeF}_6$  is presented. Using a selected ion flow tube, the thermal rate coefficients and ion product distributions have been determined at 300 K for the reactions of fourteen atomic and molecular cations, namely  $\text{H}_3\text{O}^+$ ,  $\text{CF}_3^+$ ,  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{F}^+$  and  $\text{Ne}^+$  (in order of increasing recombination energy), with  $\text{SeF}_6$  and  $\text{TeF}_6$ . The results are compared with those from the reactions of these ions with  $\text{SF}_6$ , for which the reactions with  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{N}_2\text{O}^+$  and  $\text{F}^+$  are reported for the first time. Several distinct processes are observed amongst the large number of reactions studied, including dissociative charge transfer, and  $\text{F}^-$ ,  $\text{F}$ ,  $\text{F}_2^-$  and  $\text{F}_2$  abstraction from the neutral reactant molecule to the reagent ion. The dissociative charge transfer channels are discussed in relation to vacuum ultraviolet photoelectron and threshold photoelectron-photoion coincidence spectra of  $\text{XF}_6$  ( $\text{X} = \text{S}, \text{Se}, \text{and Te}$ ). For reagent ions whose recombination energies lie between the first dissociative ionisation limit,  $\text{XF}_6 \rightarrow \text{XF}_5^+ + \text{F} + \text{e}^-$ , and the onset of ionisation of the  $\text{XF}_6$  molecule, the results suggest that if dissociative charge transfer occurs, it proceeds via an intimate encounter. For those reagent ions whose recombination energies are greater than the onset of ionisation, long-range electron transfer may occur depending on whether certain physical factors apply, for example non-zero Franck-Condon overlap. From the reaction kinetics, limits for the heats of formation of  $\text{SeF}_4$ ,  $\text{SeF}_5$ ,  $\text{TeF}_4$  and  $\text{TeF}_5$  at 298 K have been obtained;  $\Delta_f H^\circ(\text{SeF}_4) < -369 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{SeF}_5) < -621 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{TeF}_4) > -570 \text{ kJ mol}^{-1}$ , and  $\Delta_f H^\circ(\text{TeF}_5) < -822 \text{ kJ mol}^{-1}$ .

## 1. Introduction

There have been a number of studies investigating the reactions of various cations with  $\text{SF}_6$ .<sup>1-6</sup> These studies have been explorations of fundamental ion-molecule chemistry,<sup>1-4</sup> and have addressed important questions in applied sciences, such as the possible effects of ion reactions on the atmospheric lifetime of  $\text{SF}_6$  and the use of  $\text{SF}_6$  in industrial plasma processes.<sup>5,6</sup> In contrast, no information is available on the positive ion chemistry of the homologous molecules  $\text{SeF}_6$  and  $\text{TeF}_6$ . Here we report the first study of the positive ion chemistry of  $\text{SeF}_6$  and  $\text{TeF}_6$ . An objective of this study is to explore the nature of the reaction ion chemistry as the central atom in a hexafluoride molecule is changed. Differences in the reaction dynamics and kinetics may shed light on the ion chemistry occurring in  $\text{SF}_6$ -containing plasmas.<sup>6</sup> Furthermore, this study is of fundamental interest in the interpretation and understanding of ion-molecule reactions.

In this paper, the thermal (298 K) reactions of fourteen ions, spanning a range of recombination energies (6.37 – 21.56 eV), namely, and in order of increasing recombination energy,  $\text{H}_3\text{O}^+$ ,  $\text{CF}_3^+$ ,  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{F}^+$ , and  $\text{Ne}^+$ , with  $\text{SeF}_6$  and  $\text{TeF}_6$  are presented. In addition, the reactions of  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{N}_2\text{O}^+$ , and  $\text{F}^+$  with  $\text{SF}_6$  have been investigated for the first time. Reaction rate coefficients and product ion distributions are reported. For completeness and for ease of comparison, the reactions of the other ions with  $\text{SF}_6$ , which have been previously studied,<sup>1-6</sup> are presented here. Of these, the reactions of  $\text{H}_3\text{O}^+$ ,  $\text{CF}_3^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ , and  $\text{Ne}^+$  with  $\text{SF}_6$  have been reinvestigated in this study, and here there is good agreement in both the rate coefficients and the product ion branching ratios with those obtained in the other studies.

The large range of recombination energies of the reagent ions used in this study ensures that varied and interesting reactions occur. For example, charge (electron) transfer will only be energetically possible for those ions having recombination energies greater than the first dissociative ionisation limit of the  $\text{XF}_6$  molecule ( $\text{X} = \text{S}, \text{Se}$  or  $\text{Te}$ ),  $\text{XF}_6 \rightarrow \text{XF}_5^+ + \text{F} + \text{e}^-$ . The first dissociative ionisation limit is used because threshold photoelectron-photoion coincidence (TPEPICO) studies show that the ground state of  $\text{XF}_6^+$  is not a stable ion and dissociates to  $\text{XF}_5^+ + \text{F}$ .<sup>7,8</sup> (Any bound region of the  $\text{XF}_6^+$  potential energy

surface lies well outside that accessible from the neutral  $\text{XF}_6$  ground state.) Even when (dissociative) charge transfer is energetically possible, this constraint does not necessarily guarantee that it will occur. Other reaction processes might explain the observed product ions, providing an intimate encounter of the reagent ion with the neutral molecule takes place. An intimate (short-range) encounter must take place for the reactions of those ions where charge transfer is energetically impossible. Furthermore, chemical reactions in which bonds are broken and formed might occur, such as fluorine abstraction. Examples of all the reaction processes referred to above are evident in this study, and will be discussed in section 3.

## 2. Experiment

A selected ion flow tube (SIFT) was used to measure rate coefficients and to record product ions of the reactions. The SIFT apparatus and its mode of operation have been described in detail previously,<sup>9,10</sup> so only a brief description is required here. The reagent ions were generated in an enclosed, electron impact high-pressure ion source containing an appropriate gas (Ne for  $\text{Ne}^+$ ,  $\text{CF}_4$  for  $\text{F}^+$ , Ar for  $\text{Ar}^+$ ,  $\text{N}_2$  for  $\text{N}_2^+$  and  $\text{N}^+$ , CO for  $\text{CO}^+$ ,  $\text{CO}_2$  for  $\text{CO}_2^+$  and  $\text{O}^+$ ,  $\text{N}_2\text{O}$  for  $\text{N}_2\text{O}^+$ ,  $\text{H}_2\text{O}$  for  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$ , and  $\text{C}_2\text{F}_6$  for  $\text{CF}_2^+$ ,  $\text{CF}^+$  and  $\text{CF}_3^+$ ). The reagent ions were mass selected using a quadrupole mass spectrometer, injected into a 298 K helium carrier gas at a pressure of  $\sim 0.5$  Torr, transported along the flow tube and detected by a downstream sampling orifice/mass spectrometer detection system. Reactant neutral molecules were added in controlled amounts to the ion swarm/carrier gas and the loss of the reagent ions and the appearance of product ions were monitored by the downstream detection system. The reaction rate coefficients and ion product distributions were then determined in the usual way,<sup>9-11</sup> and are considered to be accurate to  $\pm 20\%$ .

The high pressure of the gases in the ionisation source is expected to significantly quench (metastable) electronically and vibrationally excited states of many molecular ions prior to their injection into the flow tube, and that the ions are thermalised in the helium carrier gas. We have not made any independent checks to confirm whether these assumptions are correct, other than for  $\text{N}_2^+$ . For this reagent ion, we know from a previous study that a significant fraction of the  $\text{N}_2^+$  ions in the flow tube was

vibrationally excited ( $\sim 40\%$  in  $\nu = 1$ ).<sup>12</sup> Whilst it is possible that other reagent molecular ions have internal energies above thermal, no curvature was observed in any of the pseudo-first-order kinetic plots (logarithm of the reagent ion signal vs. the reactant neutral concentration). This indicates that rate coefficients are the same for reactions involving 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. The  $\text{Ar}^+$  and  $\text{Ne}^+$  ions should emerge from the high-pressure source in their ground electronic state,  $^2\text{P}_{3/2}$ . 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 their reaction rates. 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>12</sup>

Water contamination in the flow tube resulted in electron transfer from  $\text{H}_2\text{O}$  to those injected ions whose recombination energies are greater than the ionisation potential of  $\text{H}_2\text{O}$ , 12.61 eV. The resulting  $\text{H}_2\text{O}^+$  signal was always less than 3 % of the parent ion signal. Some of the  $\text{H}_2\text{O}^+$  was converted to  $\text{H}_3\text{O}^+$  in the flow tube via reaction pathway (1):



Fortunately, the reactions of  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$  with any of the three group 6B hexafluorides of this study are either insignificant or slow. In any case, the reactions of  $\text{H}_2\text{O}^+$  with  $\text{SF}_6$  and  $\text{TeF}_6$ , and  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$  with

SeF<sub>6</sub> caused no difficulty in assigning the product ions for the reaction involving the parent reagent ion.

Slightly more problematic in the data analysis was the reaction of Ne<sup>+</sup> with trace H<sub>2</sub>O, which resulted in impurity ion signals of OH<sup>+</sup> and H<sub>2</sub>O<sup>+</sup> in the flow tube at a level of about 5% and 3%, respectively, of that of Ne<sup>+</sup> via dissociative and non-dissociative charge transfer:



In addition to these two ion products, HeNe<sup>+</sup> ions were formed in the flow tube from termolecular reactions of Ne<sup>+</sup> with the He buffer gas:



This led to a HeNe<sup>+</sup> signal of about 2% of the Ne<sup>+</sup> signal. For the reasons given above, the reactions of H<sub>2</sub>O<sup>+</sup> (from trace H<sub>2</sub>O) with XF<sub>6</sub> (X = S, Se, or Te) do not need to be taken into account. We have not made any allowances for the reactions of HeNe<sup>+</sup> and OH<sup>+</sup> with the neutral molecules of this study.

However, given the low percentage of these impurity ions, they are unlikely to greatly affect the product ion branching ratios associated with the reactions of Ne<sup>+</sup> will not be significantly different compared with that for the other reactions of this study.

Samples of the three compounds investigated in this study were purchased from Fluorochem Limited, Derbyshire, UK, with the following stated purities: sulphur hexafluoride (99+%), selenium hexafluoride (99%) and tellurium hexafluoride (99+%). They were used directly without additional purification.

### 3. Results and Discussion

The experimentally recorded reaction rate coefficients,  $k_{exp}$ , the product ions, and their branching ratios are given in Tables 1-3 for SF<sub>6</sub>, SeF<sub>6</sub> and TeF<sub>6</sub>, respectively. The reagent ions are listed (top to bottom) in order of decreasing recombination energy (RE) in units of electron volts (eV). Also presented in the tables are the calculated collisional rate coefficients,  $k_c$ , determined according to the Langevin equation for non-polar molecules.<sup>13</sup> Input data to these calculations include the polarizability,  $\alpha$ , of the neutral reactant molecule;  $\alpha(\text{SF}_6) = 6.54 \times 10^{-24} \text{ cm}^3$ ,  $\alpha(\text{SeF}_6) = 7.33 \times 10^{-24} \text{ cm}^3$ , and  $\alpha(\text{TeF}_6) = 9.00 \times 10^{-24} \text{ cm}^3$ .<sup>14</sup>

The determination of reaction pathways requires knowledge of the ion and neutral products, and their associated thermochemical data. Thus, an identification of both the ion and neutral products is ideally required. In our experiments this is not possible, because we can only measure the masses of the ion products and their relative intensities. Nevertheless, we can normally make some progress towards the above goal by invoking mass balance and thermochemical arguments. Consideration of the effects of enthalpy on the rate coefficients of reactions between thermalised reactants shows that, unless the reaction has  $\Delta_r H^\circ < 0$ ,  $k_{exp}$  will be less than  $k_c$ . Further if  $\Delta_r H^\circ > 20 \text{ kJ mol}^{-1}$ , then at 298 K the reaction channel will be too slow for the ion product to be detected in our SIFT apparatus. In generating a list of possible pathways to an observed ion product we normally exclude any pathway for which  $\Delta_r H^\circ > 0$ . This analysis is restricted to considerations of enthalpy, and we have ignored possible entropic effects.<sup>15</sup> Entropic factors will oppose the endothermicity for reactions in which there is an increase in the number of species between reactants and products, and we note that for most of the reactions in this study there is either no change or an increase of one or two. However, entropy effects are only likely to be significant if the enthalpy change of a reaction is close to zero. In the text, errors in the enthalpies of reaction are only given for those which are close to thermoneutral.

SF<sub>6</sub> is an important molecule, used in industrial plasmas and as an insulator to inhibit high voltage electrical breakdown. Thus, the thermochemistry of this molecule and its fragments in both neutral and cationic form is reasonably well established.<sup>16</sup> The one exception is the enthalpy of formation of SF<sub>5</sub><sup>+</sup> where a huge range of values spanning over 100 kJ mol<sup>-1</sup> exist in the literature.<sup>17</sup> We use a value for



$\Delta_f H^\circ(\text{SF}_5^+)$  of  $52 \text{ kJ mol}^{-1}$ , corresponding to a dissociative ionisation energy for  $\text{SF}_6 \rightarrow \text{SF}_5^+ + \text{F} + \text{e}^-$  of  $14.0 \text{ eV}$ , for reasons explained elsewhere.<sup>8,18</sup> Our value is  $41 \text{ kJ mol}^{-1}$  higher than that quoted in the NIST website.<sup>16</sup> This difference, however, is not sufficient to change the sign of  $\Delta_r H^\circ$  for reactions producing  $\text{SF}_5^+$  as the product ion. In other words, our interpretation of the mechanisms of reactions which form  $\text{SF}_5^+$  is not dependent on which value of  $\Delta_f H^\circ(\text{SF}_5^+)$  is used. The heats of formation of the reagent ions are well established except for  $\text{CF}_3^+$ . The value of the ionisation energy of the  $\text{CF}_3$  radical, and hence  $\Delta_f H^\circ(\text{CF}_3^+)$ , was reviewed recently,<sup>19</sup> and we use the value proposed there for  $\Delta_f H^\circ(\text{CF}_3^+)$  of  $+386 \text{ kJ mol}^{-1}$ . With these two caveats we can therefore calculate the enthalpy changes of all reactions involving  $\text{SF}_6$ .

By contrast, there is less information about the thermochemistry and ion energetics of  $\text{SeF}_6$  and  $\text{TeF}_6$ . Potts et al. have recorded the vacuum ultraviolet photoelectron spectra (VUV PES) of  $\text{SeF}_6$  and  $\text{TeF}_6$ ,<sup>20</sup> and Addison et al. the VUV PES of  $\text{SeF}_6$ .<sup>21</sup> From these PES, the ionisation potentials of various ionic states of  $\text{SeF}_6$  and  $\text{TeF}_6$  can be determined. However, such information is of limited use to analyse the ion chemistry of these molecules. Adiabatic ionisation potentials, dissociative ionisation limits, details on the decay mechanisms of the various ionic states, and enthalpies of formation of the fragment ions are all needed. To help with the analysis of this ion-molecule investigation, we have recently recorded TPEPICO spectra of  $\text{SeF}_6$  and  $\text{TeF}_6$ .<sup>8</sup> From the data dissociative ionisation limits have been determined. Furthermore, heats of formation of  $\text{SeF}_3^+$ ,  $\text{SeF}_4^+$ ,  $\text{SeF}_5^+$ ,  $\text{TeF}_3^+$ ,  $\text{TeF}_4^+$ , and  $\text{TeF}_5^+$  have been derived to be  $368 \pm 28$ ,  $426 \pm 36$ ,  $166 \pm 52$ ,  $380 \pm 28$ ,  $428 \pm 36$ , and  $4 \pm 62 \text{ kJ mol}^{-1}$ , respectively. Together with  $\Delta_f H^\circ(\text{SeF}_6) = -1117 \pm 21 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{TeF}_6) = -1318 \pm 21 \text{ kJ mol}^{-1}$ ,<sup>22</sup> these heats of formation have been used to calculate the enthalpies of various reaction pathways reported in this study. Dissociative ionisation limits are used to determine if charge transfer is energetically possible.

TPEPICO data are useful not only for determining thermodynamic information for the analysis of positive ion charge transfer data, but also for comparing product ion branching ratios at energies consistent with the recombination energy of the reagent ion. Differences observed in the product ion branching ratios may indicate that a short-range ion-molecule reaction involving an intimate encounter, rather than a long-range electron jump, has occurred. The recent studies of the charge-transfer reactions of  $\text{CCl}_4$  and  $\text{SF}_6$ ,<sup>6</sup>

and of several saturated and unsaturated perfluorocarbons,<sup>23</sup> show how the comparison of TPEPICO and flow tube data can lead to a better fundamental understanding of the reactions. Photoionisation studies are conducted at much lower pressures than flow-tube investigations of charge-transfer reactions. Differences can arise between product ion branching ratios from these two approaches when the unimolecular fragmentation of the initially formed parent ion is fast compared to the timescale of the experiment, but slow compared to the rate of collisional stabilisation. Evidence for this has been found in recent studies of charge-transfer reactions of benzene<sup>24</sup> and naphthalene<sup>25</sup>. Both these molecules have stable, bound parent molecular ions, and the rate of fragmentation above the dissociation threshold is well described by statistical theories. In contrast, there is no evidence for the existence of stable  $\text{XF}_6^+$  ions, once formed these ions are expected to dissociate very rapidly over a repulsive potential energy surface. The product ion branching ratios for charge-transfer reactions of  $\text{XF}_6$  are thus not expected to be sensitive to the buffer gas or the timescale of the experiment, and instead differences compared to photoionisation studies reflect the details of the dynamics of the encounter between  $\text{XF}_6$  and the reagent ion.

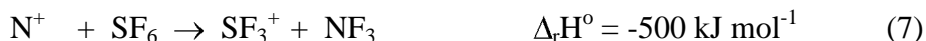
### 3.1 $\text{SF}_6$ Reactions

The rate coefficients and product ion distributions for the reactions of  $\text{H}_3\text{O}^+$ ,  $\text{CF}_3^+$ ,  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{F}^+$ , and  $\text{Ne}^+$  with  $\text{SF}_6$  are shown in Table 1. With the exception of the reactions of  $\text{H}_2\text{O}^+$  and  $\text{Ne}^+$ , the dominant product ion is  $\text{SF}_5^+$ . This is illustrated in figure 1 for the reaction of  $\text{F}^+$  with  $\text{SF}_6$ , for which two ion products are observed,  $\text{SF}_3^+$  (10%) and  $\text{SF}_5^+$  (90%). The dissociative ionisation limit to form  $\text{SF}_5^+$  from  $\text{SF}_6$  ( $\text{SF}_6 \rightarrow \text{SF}_5^+ + \text{F} + \text{e}^-$ ) has been determined to be  $14.0 \pm 0.1$  eV.<sup>18</sup> Therefore, all reagent ions with recombination energies greater than this value, i.e.  $\text{CO}^+$ ,  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{F}^+$  and  $\text{Ne}^+$ , can energetically dissociatively charge transfer to  $\text{SF}_6$ . However, the photoionisation cross section for  $\text{SF}_6$  is negligible at 14.0 eV. It is only at 15.33 eV that the photoionisation cross section becomes significant leading to an observed signal.<sup>7,8</sup> This means that for the reactions involving  $\text{CO}^+$  and  $\text{N}^+$ , dissociative charge transfer (if it occurs) can only do so by a short-range rather than a long-range mechanism.<sup>4,6,12,23,26-30</sup> A long-range mechanism requires energy resonance with non-zero Franck-Condon

factors and no distortion of the potential energy curves, with all the available energy going into fragmentation. For a short-range charge transfer, an intimate complex is formed within which chemical reaction pathways become available, i.e. bonds may be broken and formed. In the case of the reactions with  $\text{CO}^+$  and  $\text{N}^+$ , these chemical pathways would involve F abstraction from  $\text{SF}_6$  to form the observed  $\text{SF}_5^+$  product:



In agreement with the proposed short-range interaction, the minor product  $\text{SF}_3^+$  (2%) observed for the reaction with  $\text{N}^+$  requires an intimate interaction to make the overall reaction exothermic, involving either the formation of  $\text{F}_2$  and  $\text{NF}$  (Williams et al.<sup>6</sup>) or  $\text{NF}_3$ :



We note that the dissociative charge transfer channel leading to  $\text{SF}_3^+$  is endothermic:

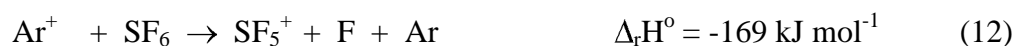


Reaction pathways (9) and (10) involving F abstraction, whilst exothermic, are not observed:



We note that the products of reactions (4) and (9) for the  $\text{CO}^+ + \text{SF}_6$  reaction differ only in where the positive charge resides. The absence of reaction pathway (9) is surprising. Reaction (9) is more exothermic than (4) since the ionisation energy of FCO is less than that of  $\text{SF}_5$ , yet all the reactive flux goes through the less exothermic channel. For the  $\text{N}^+ + \text{SF}_6$  reaction, the absence of the  $\text{NF}^+ + \text{SF}_5$  exit channel is easier to explain on energetic grounds.

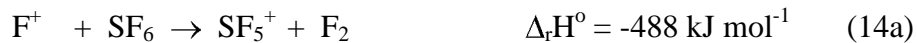
Of the four other reagent ions reported in this study which can exothermically charge transfer with  $\text{SF}_6$ , the recombination energies of  $\text{N}_2^+$  and  $\text{Ar}^+$  are resonant with the  $\tilde{X}$  ionic state of  $\text{SF}_6$ . From this, and the high efficiency of the  $\text{N}_2^+$  and  $\text{Ar}^+$  reactions ( $k_{\text{exp}}/k_c \sim 1$ ), Williams et al.<sup>6</sup> conclude that these two reactions occur via a long-range dissociative charge transfer mechanism, resulting in the only observed ion product,  $\text{SF}_5^+$ :



In agreement with this proposed mechanism, we note that only  $\text{SF}_5^+$  is observed in the TPEPICO spectrum at photon energies corresponding to the recombination energies of  $\text{N}_2^+$  and  $\text{Ar}^+$ .<sup>7</sup>

The recombination energy of  $\text{F}^+$  (17.42 eV) lies on the high-energy shoulder of the  $\tilde{A}/\tilde{B}$  photoelectron band of  $\text{SF}_6$ .<sup>7,31</sup> We may expect that, when non-zero Franck-Condon factors are involved, a long-range (dissociative) charge transfer may take place. However, this is not conclusive in itself because other factors, such as the type of molecular orbital from which the electron is ejected, can inhibit long-range charge transfer.<sup>23</sup> In these circumstances, comparisons between TPEPICO and ion-molecule branching ratios are useful to decide if long-range charge transfer is occurring. For the  $\text{F}^+$  reaction, two product ions are observed,  $\text{SF}_5^+$  (90%) and  $\text{SF}_3^+$  (10%). By comparison, the TPEPICO data show that only  $\text{SF}_5^+$  is produced at a photon energy of 17.42 eV. Thus, if dissociative charge transfer does occur, the results suggest it occurs via an intimate complex. Within such a complex, the formation of  $\text{SF}_5^+$  (90%) and

$\text{SF}_3^+$  (10%) can either result from a short-range dissociative charge transfer channel (reaction pathway (13)) and/or through a chemical channel in which bonds are broken and formed (reaction pathway (14)):



There is no means of determining which reaction pathways dominate. A dissociative charge transfer reaction pathway involving the reagent ion  $\text{F}^+$  leading to  $\text{SF}_4^+$  is exothermic, providing  $\text{F}_2$  is eliminated from the transiently formed  $(\text{SF}_6^+)^*$ :



However, this product ion is not observed.

The reaction with  $\text{Ne}^+$  is surprisingly efficient ( $k_{\text{exp}}/k_c \sim 0.5$ ) given that the recombination energy of  $\text{Ne}^+$  (21.56 eV) lies in a region of the  $\text{SF}_6$  PES which is void of any structure, falling between the  $\tilde{D}$  and  $\tilde{E}$  ionic states of  $\text{SF}_6$ . This implies that a long-range charge transfer mechanism is not operating. Instead, dissociative charge transfer, leading to the three product ions ( $\text{SF}_3^+$  (88%),  $\text{SF}_4^+$  (2%) and  $\text{SF}_5^+$  (10%)) as illustrated in figure 2, must occur via a short-range interaction, for which Franck-Condon factors and energy resonances are unimportant:





Reactions of  $\text{SF}_6$  with reagent ions whose recombination energies are less than 15.33 eV must proceed via an intimate ion-molecule complex in which bonds are broken and formed. With the exceptions of  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$ , the dominant product ion for all of these reactions is  $\text{SF}_5^+$ , formed by abstraction of  $\text{F}^-$  from  $\text{SF}_6$  to the reagent ion within the complex:



$\Delta_r H^\circ = -182, -120, -44,$  and  $-47 \text{ kJ mol}^{-1}$  for  $\text{M} = \text{O}, \text{CF}_2, \text{CF},$  and  $\text{CF}_3$ , respectively. Ignoring entropic effects, and knowing that  $\Delta_r H^\circ$  must be negative for a reaction to proceed at close to the Langevin rate, we note that the  $\text{CF}^+ + \text{SF}_6 \rightarrow \text{SF}_5^+ + \text{CF}_2$  reaction shows that the value for the first dissociative ionisation limit of  $\text{SF}_6 \rightarrow \text{SF}_5^+ + \text{F} + \text{e}^-$  must be less than 14.45 eV. The reaction rate coefficients for  $\text{M} = \text{CO}_2$  and  $\text{N}_2\text{O}$  are substantially below collisional. This is interpreted to be a result of a weak M-F bond, leading to these reactions being slightly endothermic.

The reaction of  $\text{H}_2\text{O}^+$  with  $\text{SF}_6$  has been reported by Williams et al.,<sup>6</sup> and is clearly intimate in nature, requiring bond breaking and making; the product ions observed being  $\text{OSF}_4^+$ ,  $\text{OHSF}_5^+$ , and  $\text{H}_2\text{OSF}_6^+$ , but we note no branching ratios were reported by Williams et al. This is the first report of an ion reacting with  $\text{SF}_6$  to give a product ion other than of the type  $\text{SF}_n^+$ . In this study we have also observed one other reaction which did not result in an  $\text{SF}_n^+$  product, namely the reaction of  $\text{CF}^+$  with  $\text{SF}_6$  leading to the  $\text{CF}_3^+$  product with a branching ratio of 5%:



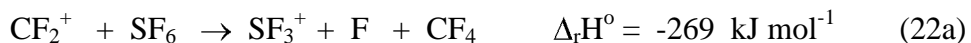
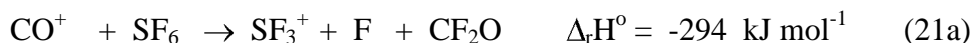
The corresponding  $\text{F}_2^-$  abstraction channel is endothermic:



and is not observed. For reactions involving the other ions with recombination energies less than 14.0 eV, in addition to the observed reaction pathway (17), other more exothermic reaction pathways are available. These include F-atom abstraction, for examples reaction pathways (9), (10) and (20):

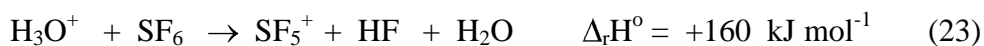


and  $\text{F}_2^-$  abstraction reactions, for examples reaction pathways (21) and (22):



However, none of these channels are observed. As is commonly observed in ion-molecule reactions, this illustrates that exothermicity alone does not drive a reaction pathway, and other factors, such as potential energy barriers due to atomic rearrangements, may dominate the dynamics of an ion-molecule reaction.

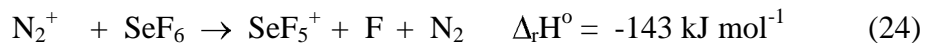
$\text{H}_3\text{O}^+$  (the recombination energy of which corresponds to  $\text{H}_3\text{O}^+ + \text{e}^- \rightarrow \text{H}_2\text{O} + \text{H}$ ) is unreactive with  $\text{SF}_6$ , in agreement with the two previous studies<sup>3,6</sup> and the thermochemistry. For example, the following reaction pathway is endothermic:



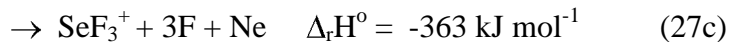
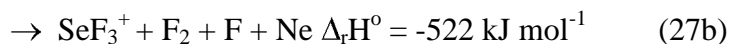
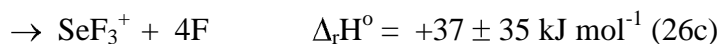
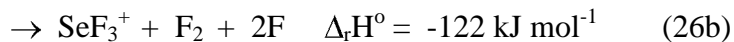
### 3.2 $\text{SeF}_6$ Reactions

The reactions of the ions with  $\text{SeF}_6$  are similar to those of  $\text{SF}_6$ , in that the majority result in  $\text{SeF}_5^+$  being the dominant product ion (Table 2). Atomic selenium has more isotopes than sulphur. A high-resolution mass spectrum of the  $\text{SeF}_5^+$  product ion is illustrated in figure 3, which identifies the various isotopes in their correct abundance.<sup>14</sup> This unambiguously identifies the peak in the mass spectrum. Only for the reactions of  $\text{Ne}^+$ ,  $\text{CO}^+$ ,  $\text{CF}_2^+$ , and  $\text{CF}_3^+$  with  $\text{SeF}_6$  is  $\text{SeF}_5^+$  not the dominant product ion.

Using TPEPICO time-of-flight spectroscopy to determine the kinetic energy released in fragmentation over a range of energies, a value of  $14.1 \pm 0.5$  eV for the first dissociative ionisation energy ( $\text{SeF}_6 \rightarrow \text{SeF}_5^+ + \text{F} + \text{e}^-$ ) has been determined.<sup>8</sup> However, the first onset of signal in the threshold photoelectron spectrum occurs at 15.3 eV. Thus, although all ions having recombination energies greater than 14.1 eV can exothermically dissociatively charge transfer with  $\text{SeF}_6$ , only those with recombination energies greater than 15.3 eV are capable of doing so by a long-range mechanism. The recombination energies of  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{F}^+$  and  $\text{Ne}^+$  all lie in regions of the  $\text{SeF}_6$  PES in which resonances are observed,<sup>20,21</sup> i.e. non-zero Franck-Condon factors connect the ground electronic state of  $\text{SeF}_6$  to its various ionic states at the recombination energies of these ions, a necessary condition for long-range charge transfer to occur. The branching ratios obtained in the ion-molecule study are identical to those obtained in our TPEPICO measurements at the recombination energies of the  $\text{N}_2^+$  and  $\text{Ar}^+$  reagent ions.<sup>8</sup> At the recombination energies of  $\text{F}^+$  and  $\text{Ne}^+$ , however, small differences in the branching ratios are observed (figure 4). Although small, these differences are significant, i.e. changes from zero in the TPEPICO results to a few percent in the ion-molecule results. Together with the observation that for these reactions  $k_{\text{exp}} \sim k_{\text{c}}$ , these observations imply a long-range dissociative charge transfer mechanism for the reactions with  $\text{N}_2^+$  and  $\text{Ar}^+$ , and an efficient short-range dissociative charge transfer mechanism for the reactions with  $\text{F}^+$  and  $\text{Ne}^+$ , leading to the observed product ions:







That a short-range charge transfer is suggested for reaction pathways (26) and (27) illustrates that energy resonance is a necessary but not sufficient criterion for long-range charge-transfer to occur. A recent study by us investigating charge-transfer from neutral perfluorocarbons to various cations suggests that the electron involved in an efficient long-range charge-transfer must be removed from a molecular orbital that is not shielded from the approaching reagent cation by other molecular orbitals of the reactant molecule.<sup>23</sup> It is possible that this is the case for molecular orbitals where electron removal results in the  $\tilde{C}$  and  $\tilde{E}$  ionic states of  $\text{SeF}_6$  at 17.42 eV and 21.56 eV, respectively.

Since the uncertainty in the first dissociative ionisation energy of  $\text{SeF}_6 \rightarrow \text{SeF}_5^+ + \text{F} + \text{e}^-$  is as large as  $\pm 0.5$  eV,  $\text{N}^+$ ,  $\text{CO}^+$ ,  $\text{CO}_2^+$  and  $\text{O}^+$  reagent ions may also have enough energy to lead to charge transfer with  $\text{SeF}_6$ ,  $(\text{SeF}_6^+)^* \rightarrow \text{SeF}_5^+ + \text{F}$ . Given that the recombination energies of these reagent ions are significantly below the observed onset of ionisation (15.3 eV), we suggest that if charge transfer does occur, it will take place within an ion-molecule complex. Within such a complex, charge transfer can compete with chemical reaction pathways in which new bonds are formed, leading not only to  $\text{SeF}_5^+$  but the other observed ion products. For the reactions of those ions whose recombination energies are less than the first dissociative ionisation energy,  $\text{N}_2\text{O}^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{CF}_2^+$ ,  $\text{CF}^+$ , and  $\text{CF}_3^+$ , the  $\text{SeF}_5^+$  product ion must result from an intimate interaction in which a fluorine anion is abstracted from  $\text{SeF}_6$  and forms a bond with the reagent ion, identical to reaction pathway (17) for  $\text{SF}_6$ :



We note that  $\Delta_f H^\circ = -345, -131, -173, -111, -35 \pm 56$ , and  $-38 \pm 56$  kJ mol<sup>-1</sup> for M = N, CO, O, CF<sub>2</sub>, CF, and CF<sub>3</sub>, respectively. We also note that the rate coefficient for reaction (28) is significantly less than collisional for M = CO<sub>2</sub> and N<sub>2</sub>O. As before, this probably indicates that the bond strengths of CO<sub>2</sub>-F and N<sub>2</sub>O-F are too weak to make the F<sup>-</sup> abstraction exothermic, or in the case of the reaction with CO<sub>2</sub><sup>+</sup> that dissociative charge transfer is slightly endothermic ( $\Delta_r H^\circ = +31$  kJ mol<sup>-1</sup>). Similarly, the slow reaction with H<sub>2</sub>O<sup>+</sup> implies that the reaction channel leading to SeF<sub>5</sub><sup>+</sup> is endothermic, in agreement with the thermochemistry, for example:



In addition to SeF<sub>5</sub><sup>+</sup>, other ion products are observed for the reactions of SeF<sub>6</sub> with CO<sup>+</sup>, CF<sub>2</sub><sup>+</sup> and CF<sup>+</sup>. For the reaction of CO<sup>+</sup>, the dominant product ion is FCO<sup>+</sup> (52%), which results from neutral fluorine abstraction:



implying that  $\Delta_f H^\circ(\text{SeF}_5) < -621$  kJ mol<sup>-1</sup>. This value is consistent with the bond dissociation energy, D<sub>0</sub>(SeF<sub>5</sub>-F), of 3.15 eV,<sup>32,33</sup> from which a value for  $\Delta_f H^\circ(\text{SeF}_5)$  of -890 kJ mol<sup>-1</sup> is obtained. Fluorine abstraction is also observed in the reaction of CF<sub>2</sub><sup>+</sup> with SeF<sub>6</sub>, resulting in CF<sub>3</sub><sup>+</sup> being the dominant product ion with a branching ratio of 52%:

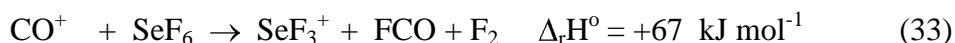


Surprisingly, the fluorine abstraction channel was not observed for the reactions of CO<sup>+</sup> and CF<sub>2</sub><sup>+</sup> with SF<sub>6</sub>, although the reaction pathways (9) and (20) are extremely exothermic.

One other ion product observed from the reaction of  $\text{CO}^+$  with  $\text{SeF}_6$  is  $\text{SeF}_3^+$  (14%), which results from  $\text{F}_2^-$  abstraction and F elimination:



The corresponding  $\text{F}^-$  abstraction and  $\text{F}_2$  elimination channel is endothermic:



The  $\text{F}_2^-$  abstraction channel leading to  $\text{SeF}_4^+$ , whilst exothermic, is not observed:



Energetically allowed pathways for the reaction of  $\text{CF}_2^+$  with  $\text{SeF}_6$  also involve  $\text{F}_2^-$  abstraction with (reaction pathway (35a)) or without (reaction pathway (35b)) fluorine elimination:



However, although these two reactions are highly exothermic, neither  $\text{SeF}_3^+$  nor  $\text{SeF}_4^+$  are observed ion products from the reaction of  $\text{CF}_2^+$  with  $\text{SeF}_6$ .

$\text{F}_2$  abstraction occurs in the reaction of  $\text{CF}^+$  with  $\text{SeF}_6$  (as is also found for the reaction of  $\text{CF}^+$  with  $\text{SF}_6$ , reaction pathway (18)) leading to the observed  $\text{CF}_3^+$  product ion:



We note that a much larger branching ratio is associated with the  $\text{CF}_3^+$  ion for this reaction pathway, 74%, compared to the reaction with  $\text{SF}_6$ , 5%. The observation of  $\text{CF}_3^+$  also suggests that  $\Delta_f H^\circ(\text{SeF}_4) < -369 \text{ kJ mol}^{-1}$ . Again, this value is consistent with the bond dissociation energy,  $D_0(\text{SeF}_4\text{-F})$  of 2.8 eV,<sup>32,33</sup> from which  $\Delta_f H^\circ(\text{SeF}_4) = -699 \text{ kJ mol}^{-1}$  is obtained.

$\text{H}_3\text{O}^+$  reacts with  $\text{SeF}_6$ , but with a reaction rate coefficient significantly below the collisional value. We were unable to unambiguously determine the product ion, being unwilling to use limited  $\text{SeF}_6$  sample for a slow reaction. Therefore, we cannot guarantee that  $\text{H}_3\text{O}^+$  was not reacting efficiently with some unknown impurity in the  $\text{SeF}_6$  sample. Thus, the rate coefficient,  $1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , obtained represents an upper limit.

### 3.3 $\text{TeF}_6$ Reactions

Compared to  $\text{SF}_6$  and  $\text{SeF}_6$ , fewer of the reagent ions react with  $\text{TeF}_6$ , but those that do generally show a richer ion chemistry than observed for the corresponding reactions with  $\text{SF}_6$  and  $\text{SeF}_6$ , as is illustrated in Table 3. For ions whose recombination energies are greater than 14.5 eV, the dominant product ion (with the exception of the  $\text{Ne}^+$  reaction) is  $\text{TeF}_5^+$ . Our recent TPEPICO study indicates that the dissociative ionisation limit of  $\text{TeF}_6$ , leading to  $\text{TeF}_5^+ + \text{F} + \text{e}^-$ , occurs at  $14.5 \pm 0.6 \text{ eV}$ .<sup>8</sup> However, the cross section for photodissociative ionisation at this energy is zero; the onset of signal in the TPES occurs at  $15.4 \pm 0.2 \text{ eV}$ . Therefore, dissociative charge transfer from  $\text{N}^+$ , reaction pathway (37), is unlikely to take place by a long-range mechanism, which as mentioned previously requires energy resonance with non-zero Franck-Condon factors. It seems more likely that dissociative charge transfer takes place via an ion-molecule complex in which competition with a chemical pathway, reaction pathway (38), might occur leading to the observed  $\text{TeF}_5^+$  product ion:



It is not usually possible to determine whether dissociative charge transfer has occurred or not, because no information of the neutral product(s) is obtained in the SIFT experiments.

The recombination energies of  $\text{N}_2^+$  and  $\text{Ar}^+$  lie in regions of the  $\text{TeF}_6$  PES and TPES in which resonances are observed.<sup>20,8</sup> Furthermore, the reactions of  $\text{TeF}_6$  with these two ions occur with unit efficiencies ( $k_{\text{exp}} = k_c$ ). Therefore, long-range dissociative charge transfer is the proposed mechanism leading to the observed ion products:



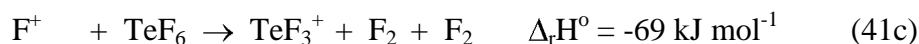
The recombination energy of  $\text{F}^+$  also lies in a region of the PES and TPES of  $\text{TeF}_6$  in which signal is observed. Therefore, long-range dissociative charge transfer is suggested given that the reaction occurs with unit efficiency. However, whilst dissociative charge transfer can explain the  $\text{TeF}_5^+$  product ion:



this mechanism cannot produce the minor  $\text{TeF}_3^+$  product ion:



$\text{TeF}_3^+$  can only occur via an intimate reaction in which  $\text{F}^-$  is transferred to the  $\text{F}^+$  reagent ion:



$\text{Ne}^+$  reacts with  $\text{TeF}_6$  via dissociative charge transfer, resulting in more product ions than observed for the other reagent ions which are energetically capable of dissociative charge transfer to  $\text{TeF}_6$ . The observed ion products are  $\text{TeF}_3^+$  (84%),  $\text{TeF}_4^+$  (4%), and  $\text{TeF}_5^+$  (12%):



The recombination energy of  $\text{Ne}^+$  lies in a structureless region of the PES and TPES of  $\text{TeF}_6$ , between the  $\tilde{E}$  and  $\tilde{F}$  ionic states.<sup>20,8</sup> Thus, there are no energy resonances connecting  $\text{TeF}_6$  to an ionic state at this energy, and therefore long-range charge transfer must be inhibited. Whilst the reaction efficiency is less than unity ( $k_{\text{exp}}/k_c \sim 0.63$ ),  $k_{\text{exp}}$  is still a significant fraction of the collisional value. We therefore assume that a reasonably efficient short-range dissociative charge transfer mechanism is occurring.

In confirmation of the proposed long-range (reactions with  $\text{N}_2^+$  and  $\text{Ar}^+$ ) and short-range (reactions with  $\text{F}^+$  and  $\text{Ne}^+$ ) charge transfer mechanisms, the TPEPICO branching ratios of  $\text{TeF}_6$  at the various reagent ion recombination energies are identical to those obtained in the ion-molecule reactions with  $\text{N}_2^+$  and  $\text{Ar}^+$ ,<sup>8</sup> and slightly but significantly different from those obtained in the reactions with  $\text{F}^+$  and  $\text{Ne}^+$  (figure 5). At the recombination energies of  $\text{F}^+$  and  $\text{Ne}^+$  only one product ion is observed in the TPEPICO spectra,  $\text{TeF}_5^+$  (at 17.4 eV) and  $\text{TeF}_3^+$  (at 21.6 eV). Such differences in the ion branching ratios may imply that a short-range charge transfer pathway (an intimate pathway) has taken place for that reaction.<sup>6,23</sup>

For the other reagent ions ( $\text{H}_3\text{O}^+$ ,  $\text{CF}_3^+$ ,  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ , and  $\text{CO}^+$ ), charge transfer is energetically impossible. These ions may then only react with  $\text{TeF}_6$  via a complex, within which bonds may be broken and formed leading to products such as obtained in reaction pathway (38). Of these ions, only  $\text{CO}^+$ ,  $\text{O}^+$  and  $\text{CF}_2^+$  are found to react efficiently with  $\text{TeF}_6$ , with  $k_{\text{exp}}$  being close to the calculated collisional value.

For the  $\text{O}^+$  reaction, only one product ion is observed,  $\text{TeF}_5^+$ , resulting from  $\text{F}^-$  abstraction from  $\text{TeF}_6$ :



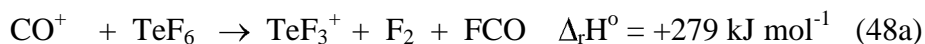
The reactions of  $\text{CO}^+$  and  $\text{CF}_2^+$  with  $\text{TeF}_6$  result in four product ions, the dominant ion being  $\text{MF}^+$  from F abstraction:



That reaction pathway (44) is observed indicates that  $\Delta_f\text{H}^\circ(\text{TeF}_5) < -822 \text{ kJ mol}^{-1}$ . The other ion products resulting from the reactions of  $\text{CO}^+$  and  $\text{CF}_2^+$  with  $\text{TeF}_6$  are the same, namely  $\text{TeF}_3^+$ ,  $\text{TeF}_4^+$ , and  $\text{TeF}_5^+$ , and these are formed with similar branching ratios (see Table 3). The only exothermic route available for the production of  $\text{TeF}_3^+$  and  $\text{TeF}_4^+$  is via  $\text{F}_2^-$  abstraction to the  $\text{CO}^+$  or  $\text{CF}_2^+$  reagent ion:



The  $\text{F}^-$  abstraction pathways, with the elimination of  $\text{F}_2$  (reaction pathways (48a) and (49a)) or the elimination of F (reaction pathways (48b) and (49b)) leading to the product ions  $\text{TeF}_3^+$  and  $\text{TeF}_4^+$ , respectively, are highly endothermic and therefore cannot occur:



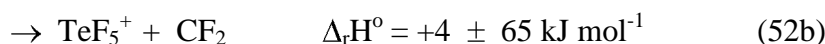


We comment that whilst the  $\text{F}_2^-$  abstraction pathways are also energetically allowed for the reactions of  $\text{CO}^+$  and  $\text{CF}_2^+$  with  $\text{SF}_6$  (reaction pathways (21) and (22)) and with  $\text{SeF}_6$  (reaction pathways (32), (34) and (35)), they also are not observed.

The  $\text{TeF}_5^+$  product ion resulting from the reactions of  $\text{CO}^+$  and  $\text{CF}_2^+$  with  $\text{TeF}_6$  occurs by  $\text{F}^-$  abstraction from  $\text{TeF}_6$  to these reagent ions in an ion-molecule complex:



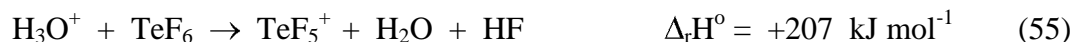
That the reagent ions  $\text{CO}_2^+$  and  $\text{N}_2\text{O}^+$  show no reaction with  $\text{TeF}_6$  suggests that the  $\text{F}^-$  abstraction channel is endothermic (again presumably due to the  $\text{CO}_2\text{-F}$  and  $\text{N}_2\text{O-F}$  bond strengths being too weak to drive the reaction). The absence of reaction of  $\text{CF}^+$  and  $\text{CF}_3^+$  with  $\text{TeF}_6$  may imply that the pathways observed in the reactions of the ions with  $\text{SF}_6$  and  $\text{SeF}_6$ , namely  $\text{F}_2$  (reaction pathway (52a)) and  $\text{F}^-$  abstraction (reaction pathways (52b) and (53)) are not energetically available:



The lack of observation of reaction pathway (52a) may imply that  $\Delta_f H^\circ(\text{TeF}_4) > -570 \text{ kJ mol}^{-1}$ . However, care must be taken in assigning heats of formation through unobserved ion-molecule channels. We have already observed that not all exothermic pathways may be followed, possibly due to a potential energy barrier inhibiting the efficiency of that pathway.



For the  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$  reagent ions, no bimolecular reactions with  $\text{TeF}_6$  were observed. This is because any obvious reaction pathways are endothermic, for examples:



An association product ion was observed with the reaction of  $\text{H}_2\text{O}^+$ ,  $(\text{H}_2\text{OTeF}_6)^+$ , for which no termolecular rate coefficient was determined because of the need to conserve the  $\text{TeF}_6$  sample.

#### 4. Concluding Remarks

The first study of the gas-phase reactions of ions with  $\text{SeF}_6$  and  $\text{TeF}_6$  has been presented in this paper. Rate coefficients and product ion distributions are reported for the reactions of fourteen atomic and molecular reagent cations. These reactions have been compared with those of  $\text{SF}_6$ , providing a better understanding of the cation chemistry of  $\text{SF}_6$ , an important additive in reactive plasmas. A wide variety of reaction processes are evident, including dissociative charge transfer, and notably various abstraction routes. Whilst there are many similarities in the reaction rate coefficients and product ion branching ratios for the reactions of the various reagent ions with  $\text{SF}_6$ ,  $\text{SeF}_6$ , and  $\text{TeF}_6$ , there are noticeable differences. Vacuum ultraviolet photoelectron and threshold photoelectron-photoion coincidence spectra have been used to help interpret the results. For the reagent ions whose recombination energies are greater than the ionisation potentials of the neutral group 6B molecules, rate coefficients and branching ratios are governed by the accessibility of ionic states. If there is no resonance feature in the PES of the neutral molecule, then (dissociative) charge transfer reactions proceed via a short-range mechanism. Differences in the ion branching ratios between those obtained in this ion-molecule study and those obtained from the TPEPICO measurements, at the recombination energy of the reagent ion, may then be apparent. We suggest that for those reagent ions whose recombination energies are greater than the lowest dissociative ionisation limit of the reactant molecule ( $\text{XF}_6 \rightarrow \text{XF}_5^+ + \text{F} + \text{e}^-$ )

but less than the observed onset of ionisation, dissociative charge transfer can only take place via an intimate encounter. Within the ion-molecule complex formed, other (chemical) reaction channels, in which bonds are broken and formed, may compete with the dissociative charge transfer channel. For reagent ions whose recombination energies are less than the lowest dissociative ionisation limit of the reactant molecule, only chemical reaction pathways are energetically favourable. Notably,  $F^-$ ,  $F$ ,  $F_2^-$  and  $F_2$  abstraction pathways have been observed.

This study represents only an initial investigation of the ion chemistry of  $SeF_6$  and  $TeF_6$ . We are extending this study, investigating other ion reactions including cations and anions. Recently, we have studied the reactions of  $O_2^-$ ,  $O^-$ ,  $OH^-$ ,  $F^-$  and  $CF_3^-$  with  $SF_6$ ,  $SeF_6$  and  $TeF_6$ , the results of which will be the subject of a forthcoming paper.

## **Acknowledgements**

We are grateful to the Technological Plasma Initiative Program, EPSRC, (grant reference: GR/L82083) for the financial support of this study. We wish to thank Ms. Elisabeth Barratt for her help in recording some of the SIFT data.

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## ***Table Captions***

Table 1. The measured 298 K reaction rate coefficients (in units of  $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and ion product branching ratios (percentages) for the reactions of the  $\text{H}_3\text{O}^+$ ,  $\text{CF}_3^+$ ,  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{F}^+$  and  $\text{Ne}^+$  with  $\text{SF}_6$ . The recombination energies (RE) in electron volts (eV) of the reagent ions are listed. The reactions with  $\text{N}^+$ ,  $\text{O}^+$ ,  $\text{H}_2\text{O}^+$  and  $\text{H}_3\text{O}^+$  have not been investigated by us, but data for these reactions are presented for completeness.<sup>1-6</sup> The Langevin (collisional) rate coefficients have been calculated,<sup>11</sup> and are shown for comparison with the experimental values. The estimated uncertainty in the measured rate coefficients and the product ion branching ratios is  $\pm 20\%$ .

Table 2. The measured 298 K reaction rate coefficients (in units of  $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and ion product branching ratios (percentages) for the reactions of the  $\text{H}_3\text{O}^+$ ,  $\text{CF}_3^+$ ,  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{F}^+$ , and  $\text{Ne}^+$  with  $\text{SeF}_6$ . The recombination energies (RE) in electron volts (eV) of the reagent ions are listed. The Langevin (collisional) rate coefficients have been calculated,<sup>11</sup> and are shown for comparison with the experimental values. The estimated uncertainty in the measured rate coefficients and the product ion branching ratios is  $\pm 20\%$ .

Table 3. The measured 298 K reaction rate coefficients (in units of  $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) and ion product branching ratios (percentages) for the reactions of the  $\text{H}_3\text{O}^+$ ,  $\text{CF}_3^+$ ,  $\text{CF}^+$ ,  $\text{CF}_2^+$ ,  $\text{H}_2\text{O}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{F}^+$ , and  $\text{Ne}^+$  with  $\text{TeF}_6$ . The recombination energies (RE) in electron volts (eV) of the reagent ions are listed. The Langevin (collisional) rate coefficients have been calculated,<sup>11</sup> and are shown for comparison with the experimental values. The estimated uncertainty in the measured rate coefficients and the product ion branching ratios is  $\pm 20\%$ .

**Table 1.**

Reagent Ion	RE (eV)	Ion Products	Branching Ratio (%)		Reaction Rate Coefficient (/10 <sup>-9</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )		
			Present	Previous	Present	Previous	Langevin
Ne <sup>+</sup>	21.56	SF <sub>3</sub> <sup>+</sup>	88	91 <sup>a</sup>	0.69	0.78 <sup>a</sup>	1.4
		SF <sub>4</sub> <sup>+</sup>	2	3			
		SF <sub>5</sub> <sup>+</sup>	10	6			
F <sup>+</sup>	17.42	SF <sub>3</sub> <sup>+</sup>	10		1.10		1.5
		SF <sub>5</sub> <sup>+</sup>	90				
Ar <sup>+</sup>	15.76	SF <sub>5</sub> <sup>+</sup>	100	100 <sup>b, c</sup>	0.91	0.93 <sup>b</sup> , 1.2 <sup>c</sup>	1.1
N <sub>2</sub> <sup>+</sup>	15.58	SF <sub>5</sub> <sup>+</sup>	100	100 <sup>a, c, d</sup>	1.03	1.2 <sup>a</sup> , 1.3 <sup>c, d</sup>	1.2
N <sup>+</sup>	14.53	SF <sub>3</sub> <sup>+</sup>		2 <sup>a</sup>		1.8 <sup>a</sup> , 1.4 <sup>c, d</sup>	1.7
		SF <sub>5</sub> <sup>+</sup>		98 <sup>a</sup> , 100 <sup>c, d</sup>			
CO <sup>+</sup>	14.01	SF <sub>5</sub> <sup>+</sup>	100	100 <sup>c, e</sup>	0.92	1.3 <sup>c</sup> , 0.98 <sup>e</sup>	1.2
CO <sub>2</sub> <sup>+</sup>	13.77	SF <sub>5</sub> <sup>+</sup>	100	100 <sup>d</sup>	0.09	0.01 <sup>d</sup>	1.0
O <sup>+</sup>	13.62	SF <sub>5</sub> <sup>+</sup>		100 <sup>c, f</sup>		1.5 <sup>c</sup> , 2.4 <sup>f</sup>	1.6
N <sub>2</sub> O <sup>+</sup>	12.89	SF <sub>5</sub> <sup>+</sup>	100		0.003		1.0
H <sub>2</sub> O <sup>+</sup>	12.61	(OSF <sub>4</sub> ) <sup>+</sup> <sup>a</sup>				0.19 <sup>a</sup>	1.5
		(OHSF <sub>5</sub> ) <sup>+</sup>	...	...			
		(H <sub>2</sub> OSF <sub>6</sub> ) <sup>+</sup>					
CF <sub>2</sub> <sup>+</sup>	11.42	SF <sub>5</sub> <sup>+</sup>	100		0.79		0.98
CF <sup>+</sup>	9.11	SF <sub>5</sub> <sup>+</sup>	95		0.88		1.2
		CF <sub>3</sub> <sup>+</sup>	5				
CF <sub>3</sub> <sup>+</sup>	≤8.8	SF <sub>5</sub> <sup>+</sup>	100	100 <sup>d</sup>	0.22	0.25 <sup>d</sup>	0.87
H <sub>3</sub> O <sup>+</sup>		No				≤0.005 <sup>d</sup>	1.5
		Reaction				≤0.002 <sup>a</sup>	

(a) Williams et al [6]

(b) Shul et al [4]

(c) Fehsenfeld [1]

(d) Babcock and Streit [3]

(e) Bowers and Chau [2]

(f) Morris et al [5]

**Table 2.**

Reagent Ion	RE (/eV)	SeF <sub>6</sub>			
		Ion Products	Branching Ratio (%)	Reaction Rate Coefficient (/10 <sup>-9</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	
				Present	Langevin
Ne <sup>+</sup>	21.56	SeF <sub>3</sub> <sup>+</sup> SeF <sub>5</sub> <sup>+</sup>	92 8	1.2	1.5
F <sup>+</sup>	17.42	SeF <sub>3</sub> <sup>+</sup> SeF <sub>5</sub> <sup>+</sup>	4 96	1.4	1.5
Ar <sup>+</sup>	15.76	SeF <sub>5</sub> <sup>+</sup>	100	1.2	1.1
N <sub>2</sub> <sup>+</sup>	15.58	SeF <sub>5</sub> <sup>+</sup>	100	1.6	1.3
N <sup>+</sup>	14.53	SeF <sub>5</sub> <sup>+</sup>	100	1.6	1.8
CO <sup>+</sup>	14.01	FCO <sup>+</sup> SeF <sub>3</sub> <sup>+</sup> SeF <sub>5</sub> <sup>+</sup>	52 14 34	1.1	1.3
CO <sub>2</sub> <sup>+</sup>	13.77	SeF <sub>5</sub> <sup>+</sup>	100	< 0.01	1.1
O <sup>+</sup>	13.62	SeF <sub>5</sub> <sup>+</sup>	100	1.5	1.6
N <sub>2</sub> O <sup>+</sup>	12.89	SeF <sub>5</sub> <sup>+</sup>	100	< 0.01	1.1
H <sub>2</sub> O <sup>+</sup>	12.61	SeF <sub>5</sub> <sup>+</sup>	100	< 0.05	1.6
CF <sub>2</sub> <sup>+</sup>	11.42	CF <sub>3</sub> <sup>+</sup> SeF <sub>5</sub> <sup>+</sup>	52 48	0.93	1.0
CF <sup>+</sup>	9.11	CF <sub>3</sub> <sup>+</sup> SeF <sub>5</sub> <sup>+</sup>	74 26	0.64	1.2
CF <sub>3</sub> <sup>+</sup>	≤8.9	SeF <sub>5</sub> <sup>+</sup>	100	0.44	0.89
H <sub>3</sub> O <sup>+</sup>		? (see text)		< 0.001	1.5

**Table 3.**

Reagent Ion	RE (/eV)	TeF <sub>6</sub>			
		Ion Products	Branching Ratio (%)	Reaction Rate Coefficient (/10 <sup>-9</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )	
				Present	Langevin
Ne <sup>+</sup>	21.56	TeF <sub>3</sub> <sup>+</sup> TeF <sub>4</sub> <sup>+</sup> TeF <sub>5</sub> <sup>+</sup>	84 4 12	1.0	1.6
F <sup>+</sup>	17.42	TeF <sub>3</sub> <sup>+</sup> TeF <sub>5</sub> <sup>+</sup>	3 97	1.7	1.7
Ar <sup>+</sup>	15.76	TeF <sub>5</sub> <sup>+</sup>	100	1.1	1.2
N <sub>2</sub> <sup>+</sup>	15.58	TeF <sub>5</sub> <sup>+</sup>	100	1.3	1.4
N <sup>+</sup>	14.53	TeF <sub>5</sub> <sup>+</sup>	100	1.7	1.9
CO <sup>+</sup>	14.01	FCO <sup>+</sup> TeF <sub>3</sub> <sup>+</sup> TeF <sub>4</sub> <sup>+</sup> TeF <sub>5</sub> <sup>+</sup>	55 20 3 22	1.3	1.4
CO <sub>2</sub> <sup>+</sup>	13.77	No Reaction			1.2
O <sup>+</sup>	13.62	TeF <sub>5</sub> <sup>+</sup>	100	1.8	1.8
N <sub>2</sub> O <sup>+</sup>	12.89	No Reaction			1.2
H <sub>2</sub> O <sup>+</sup>	12.61	(H <sub>2</sub> OTeF <sub>6</sub> ) <sup>+</sup>			1.7
CF <sub>2</sub> <sup>+</sup>	11.42	CF <sub>3</sub> <sup>+</sup> TeF <sub>3</sub> <sup>+</sup> TeF <sub>4</sub> <sup>+</sup> TeF <sub>5</sub> <sup>+</sup>	66 10 6 18	0.91	1.1
CF <sup>+</sup>	9.11	No Reaction			1.3
CF <sub>3</sub> <sup>+</sup>	≤8.9	No Reaction			0.96
H <sub>3</sub> O <sup>+</sup>		No Reaction			1.7



## Figure Captions

Figure 1. A typical mass spectrum obtained from the reaction of  $F^+$  with  $SF_6$ . Two product ions are observed,  $SF_5^+$  (dominant) and  $SF_3^+$ . The ion identified as  $SF_5OH^+$  results from reactions of the impurity ion  $H_2O^+$ , formed in the flow tube from reaction of  $F^+$  with trace  $H_2O$ , with  $SF_6$ .  $SF_5OH^+$  must be the dominant ion in this reaction, although other product ions have been observed from the reaction of  $H_2O^+$  with  $SF_6$ , for which no branching ratios are listed[6].

Figure 2. A typical mass spectrum obtained from the reaction of  $Ne^+$  with  $SF_6$ , illustrating the greater degree of fragmentation as a result of the high recombination energy of  $Ne^+$  (21.56 eV) compared to the other reagent ions used in this study. Three product ions are observed;  $SF_3^+$  (dominant),  $SF_4^+$  and  $SF_5^+$ .

Figure 3. A high-resolution mass spectrum recording of the  $SeF_5^+$  product ion (recorded here from the reaction of  $F^+$  with  $SeF_6$ ), identifying the selenium isotopes. The peak heights agree well with the relative abundance of these isotopes [14].

Figure 4. TPEPICO breakdown diagram for  $SeF_6$  compared to the cation product branching ratios obtained from the reactions of  $N_2^+$ ,  $Ar^+$ ,  $F^+$  and  $Ne^+$  with  $SeF_6$ .

Figure 5. TPEPICO breakdown diagram for  $TeF_6$  compared to the cation product branching ratios obtained from the reactions of  $N_2^+$ ,  $Ar^+$ ,  $F^+$  and  $Ne^+$  with  $TeF_6$ .

Figure 1

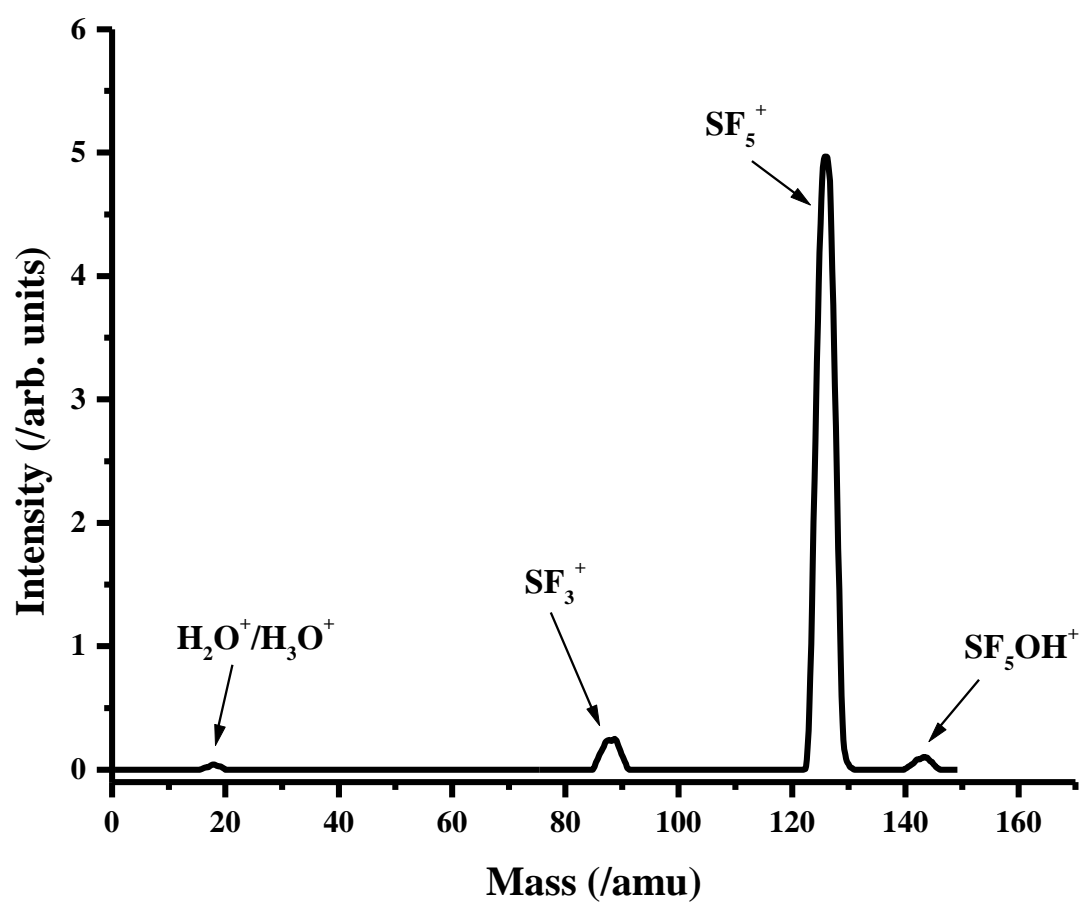


Figure 2

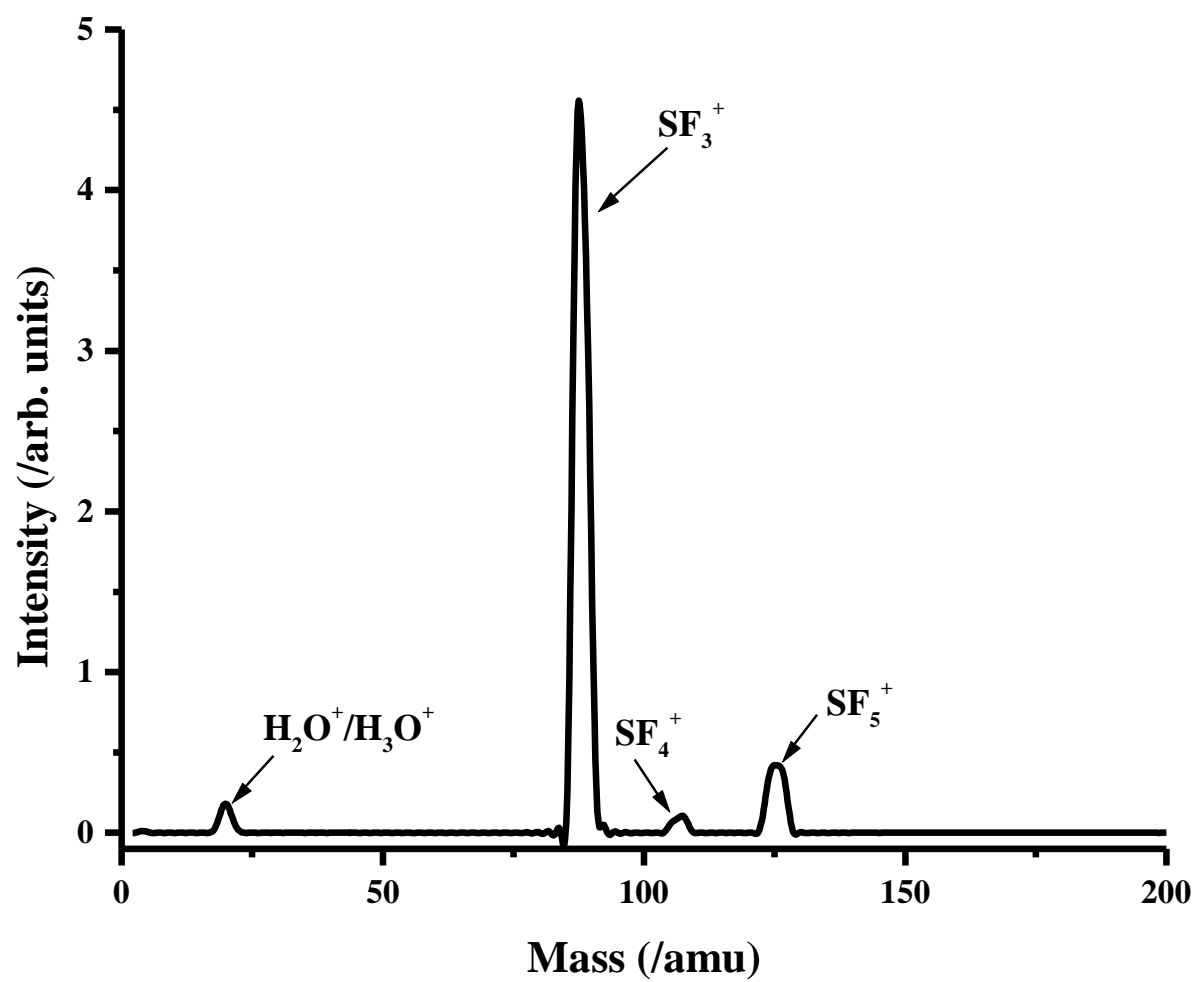
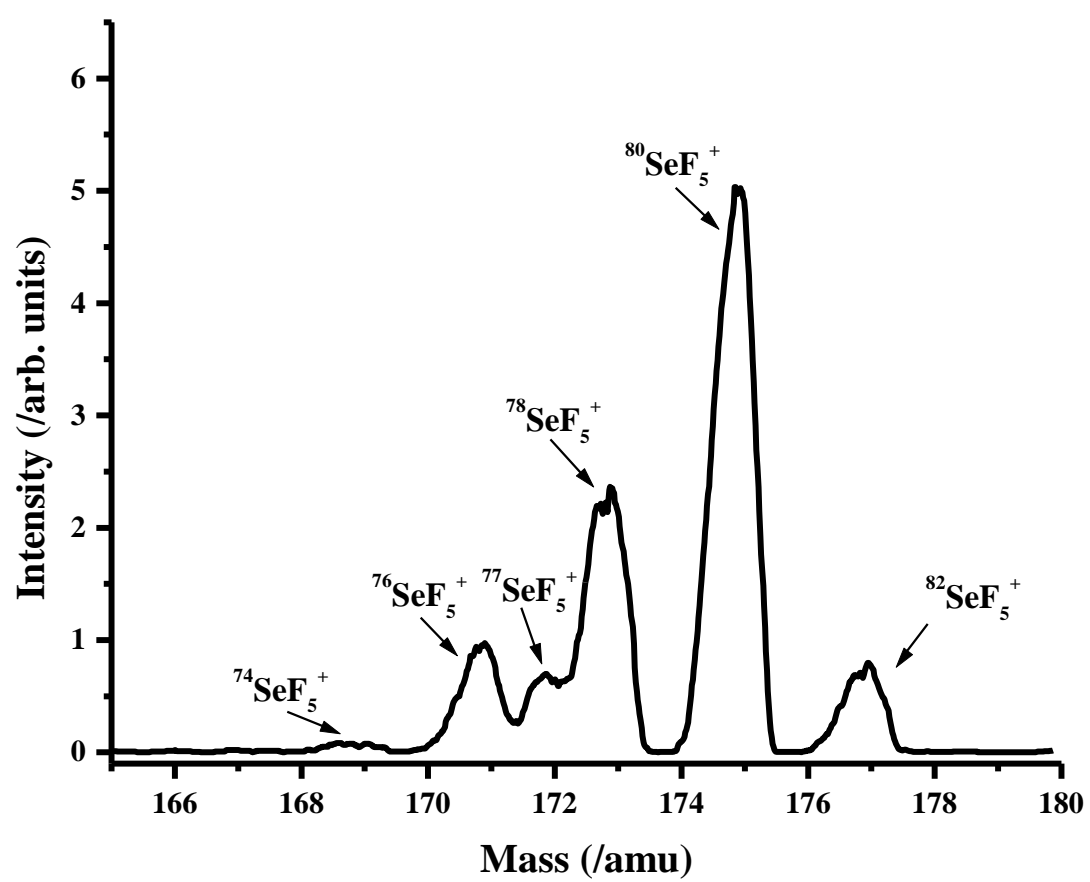
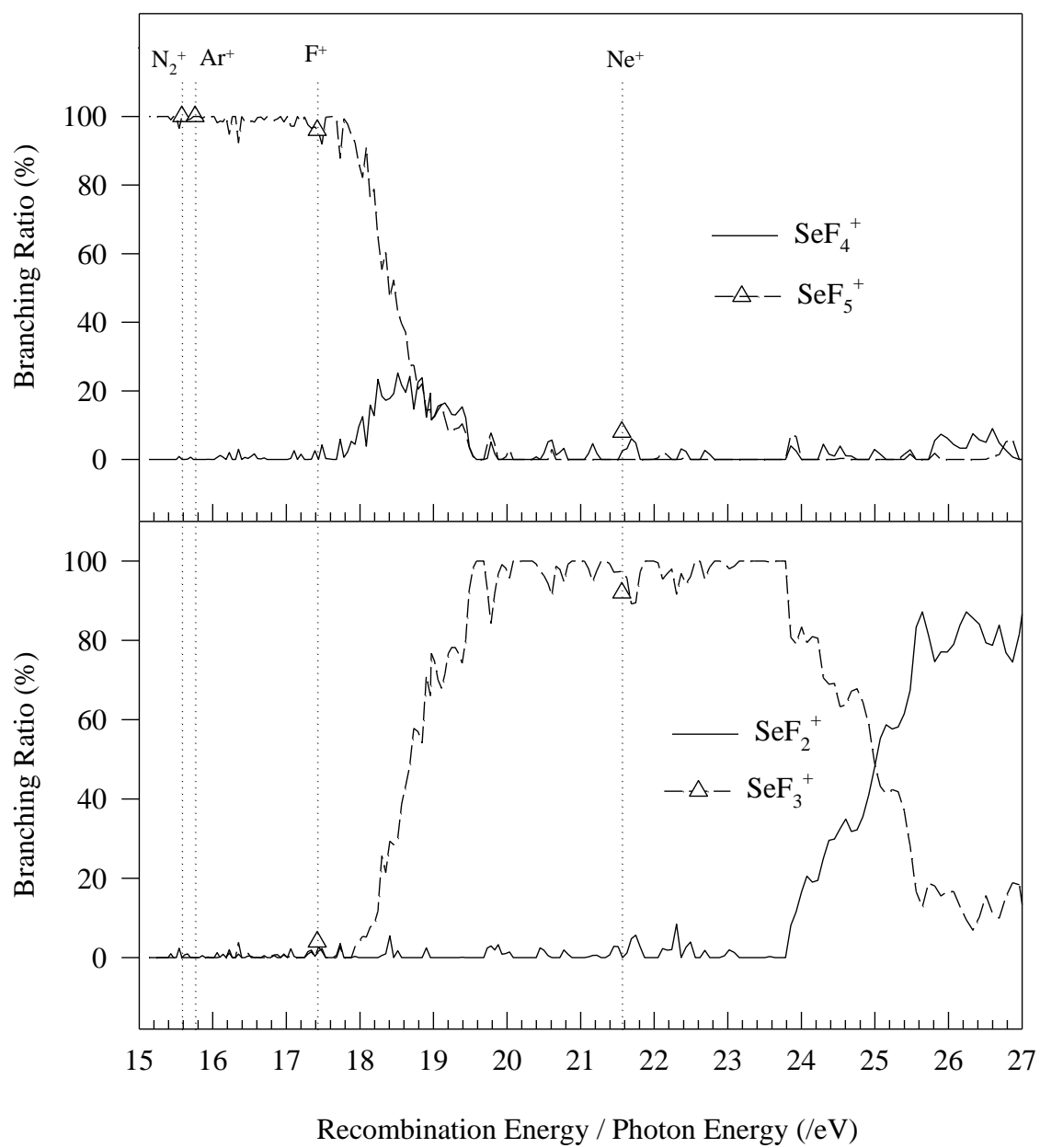


Figure 3



**Figure 4**



**Figure 5**

