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A selected ion flow tube study of the reactions of  $\text{CHCl}_2\text{F}$ ,  $\text{CHClF}_2$  and  $\text{CH}_2\text{ClF}$

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Professor Richard Tuckett (University of Birmingham) / July 2011

# A selected ion flow tube study of the reactions between gas phase cations and $\text{CHCl}_2\text{F}$ , $\text{CHClF}_2$ and $\text{CH}_2\text{ClF}$

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**Abstract** : The branching ratios and rate coefficients have been measured at 298 K for the reactions between  $\text{CHCl}_2\text{F}$ ,  $\text{CHClF}_2$  and  $\text{CH}_2\text{ClF}$  and the following cations (with recombination energies in the range 6.3 – 21.6 eV);  $\text{H}_3\text{O}^+$ ,  $\text{SF}_x^+$  ( $x = 1 - 5$ ),  $\text{CF}_y^+$  ( $y = 1 - 3$ ),  $\text{NO}^+$ ,  $\text{NO}_2^+$ ,  $\text{O}_2^+$ ,  $\text{Xe}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{Kr}^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{F}^+$  and  $\text{Ne}^+$ . The majority of the reactions proceed at the calculated collisional rate, but the reagent ions  $\text{SF}_3^+$ ,  $\text{NO}^+$ ,  $\text{NO}_2^+$  and  $\text{SF}_2^+$  do not react. Surprisingly, although all of the observed product channels are calculated to be endothermic,  $\text{H}_3\text{O}^+$  does react with  $\text{CHCl}_2\text{F}$ . On thermochemical grounds,  $\text{Xe}^+$  appears to react with these molecules only when it is in its higher-energy  $^2\text{P}_{1/2}$  spin-orbit state. In general, most of the reactions form products by dissociative charge transfer, but some of the reactions of  $\text{CH}_2\text{ClF}$  with the lower-energy cations produce the parent cation in significant abundance. The branching ratios produced in this study and by threshold photoelectron-photoion coincidence spectroscopy (preceding paper) agree reasonably well over the energy range 11 – 22 eV. In about one fifth of the large number of reactions studied the branching ratios are in excellent agreement and appreciable energy resonance between an excited state and the ground state of the ionized neutral exists, suggesting that these reactions proceed exclusively by a long-range charge transfer mechanism. Upper limits for the enthalpy of formation at 298 K of  $\text{SF}_4\text{Cl}$  ( $-637 \text{ kJ mol}^{-1}$ ),  $\text{SClF}$  ( $-28 \text{ kJ mol}^{-1}$ ) and  $\text{SHF}$  ( $-7 \text{ kJ mol}^{-1}$ ) are determined.

## 1. Introduction

The study of ion-molecule reactions is of importance in many areas of science, such as plasmas found in industrial applications and in the interstellar medium.<sup>1,2</sup> These fundamental processes underpin the complex reactivity that is evident in these systems. One such mechanism is that of charge transfer, which can occur over either a long-range or a short-range. The former model states that as an ion ( $A^+$ ) makes an approach toward a neutral reagent ( $BC$ ), the ionic charge induces a dipole interaction in the neutral. At a critical separation between the two species, the potential curves of  $A^+-BC$  and  $A-BC^+$  cross, thus allowing an electron to jump from the neutral to the ion. Factors that exhibit a marked preference for the occurrence of this process include energy resonance between the ground electronic state and an ionic state of the neutral and the extent of shielding in the molecular orbital from which the electron is removed. A guide to the possible energy resonances can be found in the photoelectron spectrum (PES) of the neutral species. For the molecular reagent cations, the Franck-Condon factor for neutralising  $A^+$  can also be important. If the long-range process is unfavourable, then the two species move closer together. The resulting intimate interaction can perturb the relevant potential surfaces to such an extent that a crossing is stimulated, thereby leading to short-range charge transfer. Note that, in this case, although the Franck-Condon factors involved are perturbed, they still need to be appreciable in the isolated molecule for this process to transpire. Short-range charge transfer can compete with chemical reactions, where bonds are broken and formed. As neither a curve crossing nor a Franck-Condon factor is required for a chemical reaction to occur, this channel can proceed efficiently. A thorough review of the aforementioned three processes has been published by our group.<sup>3</sup>

In this paper, we present a study of the dynamics and kinetics of reactions between ions of known recombination energy and  $CHCl_2F$ ,  $CHClF_2$  and  $CH_2ClF$  using the well-established selected ion flow tube (SIFT) technique. Correlation between the derived branching ratios and those obtained using tunable energy photons as the excitation source,<sup>4</sup> alongside the presence of an appreciable band in the threshold photoelectron spectrum (TPES) at the recombination energy of the reagent ion, points towards the occurrence of a long-range charge transfer mechanism. An absence of these features suggests that other processes dominate. This study is an extension of recent SIFT work performed by Mayhew and collaborators on some halogenated methanes,<sup>5</sup> in addition to previous experiments looking at reactions of the three titled molecules with the anions  $OH^-$ ,  $O^-$  and  $O_2^-$  and an electron attachment study.<sup>6-8</sup>

## 2. Experimental

The SIFT apparatus has been described in detail elsewhere.<sup>9</sup> Briefly, each reagent ion of interest was produced in a high pressure electron impact ion source containing an appropriate source gas ( $H_2O$  for  $H_3O^+$ ,  $SF_6$  for  $SF_x^+$  (where  $x = 1-5$ ),  $CF_4$  for  $CF_2^+$ ,  $CF_3^+$  and  $F^+$ ,  $C_2F_6$  for  $CF^+$ ,  $NO$  for  $NO^+$ ,  $NO_2$  for  $NO_2^+$ ,

O<sub>2</sub> for O<sub>2</sub><sup>+</sup>, Xe for Xe<sup>+</sup>, N<sub>2</sub>O for N<sub>2</sub>O<sup>+</sup>, CO for O<sup>+</sup> and CO<sup>+</sup>, CO<sub>2</sub> for CO<sub>2</sub><sup>+</sup>, Kr for Kr<sup>+</sup>, N<sub>2</sub> for N<sup>+</sup> and N<sub>2</sub><sup>+</sup>, Ar for Ar<sup>+</sup>, Ne for Ne<sup>+</sup>). The O<sub>2</sub><sup>+</sup> ions were produced using a mixture comprising a 4:1 ratio of O<sub>2</sub> and N<sub>2</sub> in order to reduce the chances of filament burnout in the ion source. Only the particular ion of interest was injected into a flow tube holding *ca.* 0.5 Torr of high purity (99.997%) helium as a buffer gas. A quadrupole mass filter performs this mass selection. The neutral reactant of choice is then admitted at the far end of the flow region, with subsequent detection of the resultant ionic products using a quadrupole mass spectrometer. The loss of reagent ion signal, alongside the increase in the various product ion signal(s), was recorded as a function of neutral reactant concentration. The amount of neutral was altered between zero and a concentration that depleted the reactant ion signal by *ca.* 90%. Plots of the logarithm of the reagent ion signal *vs.* neutral molecule concentration allowed rate coefficients to be determined from a linear least-squares fit. Rate coefficients with a lower limit of *ca.* 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> can be measured in our apparatus. Percentage branching ratios for each product ion were derived from graphs of the relative product ion counts *vs.* neutral molecule concentration, with extrapolation to zero neutral gas flow to remove any deviations due to secondary reactions. The various chlorine isotopes are accounted for in this procedure. This data can be compared to branching ratio diagrams constructed from photoionization of each of the neutral molecules<sup>4</sup> in order to shed light on the nature of charge transfer mechanisms. We quote the error in the branching ratios as ± 20% for values greater than 10%. This error increases for smaller branching ratios – indeed, the error associated with branching ratios of 1% is given as ± 100%.

Quenching of vibrationally and electronically excited ionic states should be achieved by the use of several Torr of the ion source gases. This is not strictly the case, however, as previous studies in our laboratory have shown there is *ca.* 20% population of the *v* = 1 and 2 levels of O<sub>2</sub><sup>+</sup> and *ca.* 40% in the first excited vibrational level of N<sub>2</sub><sup>+</sup>.<sup>10,11</sup> There is also a possibility of population of higher spin-orbit states within atomic ions. The spin-orbit splitting between the <sup>2</sup>P<sub>3/2</sub> ground state and the higher-energy <sup>2</sup>P<sub>1/2</sub> state in ions of the noble gases can vary in magnitude considerably; the values of interest to this work are 0.10, 0.18, 0.67 and 1.31 eV for Ne<sup>+</sup>, Ar<sup>+</sup>, Kr<sup>+</sup> and Xe<sup>+</sup>, respectively.<sup>12</sup> The F<sup>+</sup> ground state exhibits a low magnitude triplet splitting, whose three levels span an energy range of only 0.06 eV. Given the small energy enhancement that excitation to the higher states would impart, the excited states of F<sup>+</sup>, Ne<sup>+</sup> and Ar<sup>+</sup> are expected to have the same reactivity as their respective ground states. However, the larger extent of splitting for Kr<sup>+</sup> and Xe<sup>+</sup> can lead to distinct rates of reaction depending on which state the ion is in prior to reaction. Indeed, under certain circumstances the lower <sup>2</sup>P<sub>3/2</sub> state was found to react faster than the <sup>2</sup>P<sub>1/2</sub> state in reactions with molecules containing between two and five atoms (*e.g.* CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>).<sup>13</sup> The molecular reagent ions may also have some internal energy excitation, in addition to the thermal contribution expected at 298 K. However, upon inspection of the individual pseudo-first order kinetic plots, none display curvature of *ln*(reagent ion signal) *vs.* concentration of neutral co-reactant. This result

indicates one of two possibilities. Either, the rates of reactions initiated by ions that have some vibrational or spin-orbit excited population are the same as those involving ground state ions. Or, reaction is only possible from the higher-energy state. Anticipating whether the product ion branching ratios are affected is more problematic, although the small energetic increments involved in most cases are unlikely to make a radical difference to these quantities.

Residual water in the flow tube can cause problems, as removal of an electron from H<sub>2</sub>O and the subsequent reaction  $\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$  results in a signal at  $m/z = 19$  due to H<sub>3</sub>O<sup>+</sup>. This only occurs when ions with recombination energies greater than the ionisation energy of neutral water (12.62 eV) are injected. As can be seen later, H<sub>3</sub>O<sup>+</sup> only reacts with CHCl<sub>2</sub>F out of the three neutrals studied here, and is therefore only a hindrance in this case. Tuning the ion optics of the entrance quadrupole generally produced a reactant ion signal that was at least 10 times larger than that of H<sub>3</sub>O<sup>+</sup>; therefore, the smaller signal could be ignored. The impact of this problem was further reduced *via* cleaning of the He inlet line using a liquid-nitrogen-cooled zeolite trap.

### 3. Results and Discussion

#### 3.1 Rate Coefficients

The vast majority of the experimentally determined rate coefficients,  $k_{\text{exp}}$ , have values that approach the capture rate values,  $k_{\text{c}}$ , determined using modified-average dipole orientation (MADO) theory,<sup>14</sup> as shown in Tables 1 – 3. Therefore, these processes occur efficiently, in that most of the ion-molecule collisions lead to reaction. MADO theory accounts for the polar nature of these three systems by including the relevant dipole moments. These were given as 1.29, 1.42 and 1.82 D for CHCl<sub>2</sub>F, CHClF<sub>2</sub> and CH<sub>2</sub>ClF, respectively.<sup>12</sup> It also includes the polarisabilities of each molecule, the values for CHCl<sub>2</sub>F and CHClF<sub>2</sub> being 6.82 and 6.38 × 10<sup>-24</sup> cm<sup>3</sup>, respectively.<sup>12</sup> No value for the polarisability of CH<sub>2</sub>ClF has been published, so the empirical method of adding atomic hybrid components<sup>15</sup> was used to give a value of 4.48 × 10<sup>-24</sup> cm<sup>3</sup>. Of the cases where  $k_{\text{exp}} < k_{\text{c}}$ , the reactions involving SF<sub>5</sub><sup>+</sup> are the most prominent. In all three reactions,  $k_{\text{exp}}$  does not get above 60% of the capture value. This suggests that a somewhat congested collision complex is initially formed, as SF<sub>5</sub><sup>+</sup> is the bulkiest reagent ion used in this study, with short-range charge transfer and possible bond cleavage occurring subsequently. It is also worth noting that reactions of SF<sup>+</sup> and SF<sub>4</sub><sup>+</sup> with CHClF<sub>2</sub> also proceed slowly, with experimental values that are < 50% of the capture coefficients, producing CHClF<sup>+</sup> as the single ionic product.

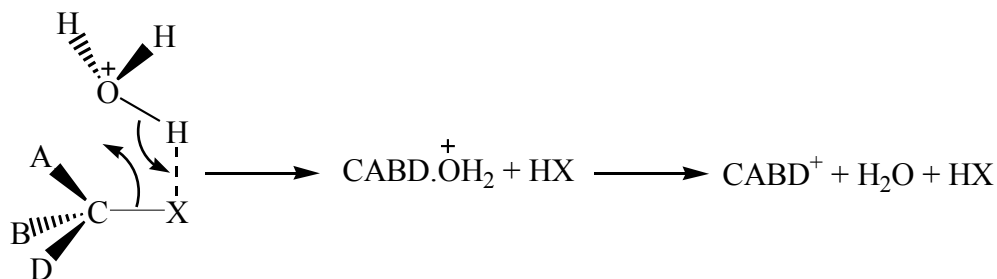
#### 3.2 Branching Ratios

##### 3.2.1 CHCl<sub>2</sub>F

The products resulting from reactions of several cations and CHCl<sub>2</sub>F are displayed in Table 1. The proposed neutral products, shown in column 4, are the species that give the lowest value for the enthalpy

of reaction at 298 K,  $\Delta_r H^\circ_{298}$ , whilst still being chemically reasonable. These values of  $\Delta_r H^\circ_{298}$  provide a quantitative guide for the occurrence of the suggested products for each reaction, and are listed in column 5. Firstly, we discuss reactions involving ions whose recombination energies are below the onset of ionisation of  $\text{CHCl}_2\text{F}$ , given as  $11.50 \pm 0.05$  eV.<sup>4</sup>

The reaction between  $\text{H}_3\text{O}^+$  and  $\text{CHCl}_2\text{F}$  results in three products, which are formed *via* hydrogen halide, or simply diatomic hydrogen, elimination. This process has been noted before by reactions between  $\text{H}_3\text{O}^+$  and halomethanes,<sup>16</sup> with the mechanism proceeding thus;



where X, A, B and D are chlorine, fluorine or hydrogen atoms. The major product, with a branching ratio of 85%, is formed by H atom loss from the neutral precursor, *i.e.* X = H. This observation can be explained by the steric effects of the transition state, as the smaller size of a hydrogen atom means that attack by  $\text{H}_3\text{O}^+$  is least hindered at this position. For this reaction to occur as above, these steps have to occur rapidly to overcome collisional stabilisation of the complex.<sup>16</sup> As the rate of this reaction is close to  $k_c$ , then we believe that these processes occur efficiently. However, all three observed reactions are appreciably endothermic. Previous work has highlighted that entropic effects can drive such seemingly unfavourable processes,<sup>17-19</sup> but the magnitudes of the endothermicities of the three processes we observe are much larger than those involved in these studies. The overall change in number of moles in the  $\text{H}_3\text{O}^+ + \text{CHCl}_2\text{F}$  reaction is +1 and we might expect an increase in entropy of the order of  $100 \text{ J mol}^{-1} \text{ K}^{-1}$ . However, even if  $\Delta_r S^\circ_{298}$  is as large as this, the  $T\Delta_r S^\circ_{298}$  term would only contribute *ca.*  $30 \text{ kJ mol}^{-1}$  at room temperature. Therefore, the  $T\Delta_r S^\circ_{298}$  term will not be large enough to compensate for the positive  $\Delta_r H^\circ_{298}$  values we calculate, and entropy alone does not seem to be a plausible explanation for our results. (Note that  $\Delta_r S^\circ_{298}$  would need to be *ca.*  $500 \text{ J mol}^{-1} \text{ K}^{-1}$  for entropy alone to explain the presence of the most abundant ion product,  $\text{CCl}_2\text{F}^+$  (85%); this huge value seems very unlikely.) It is also possible that the literature values used to calculate  $\Delta_r H^\circ_{298}$  are in error, but the only values where this is potentially the case is the product ions, and these have not caused such a significant discrepancy in any of the other reactions in this work. A mis-assignment of the ionic products, such as  $\text{CCl}_2\text{F}^+$  and  $\text{CHClF}^+$  being  $\text{CCl}_2.\text{H}_3\text{O}^+$  and  $\text{CHCl}.\text{H}_3\text{O}^+$ , can be discounted, as these proposed complex ions are chemically improbable and would require extensive rearrangement in the transition state. Additionally, such an uncertainty cannot be applied to the  $\text{CHCl}_2^+$  product. Direct proton transfer to  $\text{CHCl}_2\text{F}$  is not observed in

this reaction, which is consistent with room temperature proton affinity ( $PA_{298}$ ) data; the  $PA_{298}$  of  $\text{CHCl}_2\text{F}$  ( $676.8 \text{ kJ mol}^{-1}$ ) has been calculated using *ab initio* methods,<sup>20</sup> and is smaller than the  $PA_{298}$  of water ( $691 \text{ kJ mol}^{-1}$ ).<sup>21</sup> Therefore, the proton is more likely to reside on the water molecule. In conclusion, we are unable to explain why this reaction proceeds.

Whereas  $\text{SF}_3^+$ ,  $\text{NO}^+$ ,  $\text{NO}_2^+$  and  $\text{SF}_2^+$  do not react at an observable rate, the remaining ions that fall in this energy range react to form two major products by dissociative charge transfer, namely  $\text{CHClF}^+$  and  $\text{CHCl}_2^+$ . The former ion is dominant, being formed with branching ratios of between 92% (with  $\text{SF}^+$ ) and 61% ( $\text{CF}_2^+$ ). All of these reactions also result in a single neutral product. Therefore, Cl atom abstraction *via* a short-range complex is favoured, but removal of a fluorine atom is not insignificant. The enthalpy of formation of  $\text{SClF}$ , produced in the  $\text{SF}^+$  reaction, is unknown. Using the known thermochemistry of the other components, we ascribe this reaction as being exothermic if the unspecified quantity is less than  $-28 \text{ kJ mol}^{-1}$ . As the respective values of  $\Delta_f H^\circ_{298}$  for  $\text{SCl}_2$  and  $\text{SF}_2$  are  $-18$  and  $-295 \text{ kJ mol}^{-1}$ , this seems feasible.<sup>22,23</sup>

At ion recombination energies that are higher than the ionisation energy of  $\text{CHCl}_2\text{F}$ , long-range charge transfer becomes possible. Over the recombination energy range  $11.92 - 14.53 \text{ eV}$ , incorporating reactions with  $\text{SF}_4^+$  to  $\text{N}^+$  inclusive, the branching ratio for  $\text{CHClF}^+$  formation is close to unity. It peaks at 100% with  $\text{SF}_4^+$ , where the heat of formation of the neutral product is not known; this reaction will be exothermic if the  $\Delta_f H^\circ_{298}$  of  $\text{SF}_4\text{Cl}$  is less than  $-637 \text{ kJ mol}^{-1}$ . This number is consistent with the  $\Delta_f H^\circ_0$  value for  $\text{SF}_4\text{Cl}$  of  $-761 \text{ kJ mol}^{-1}$  determined in previous SIFT work by our group on  $\text{SF}_5\text{Cl}$ .<sup>24</sup> Another set of proposed neutrals is  $\text{SF}_4 + \text{Cl}$ , and if the well-established thermochemistry of these neutrals is used, this reaction is just exothermic. For the reaction with  $\text{O}_2^+$ ,  $\text{CHClF}^+$  can form with either  $\text{ClOO}$  or  $\text{OCIO}$  on enthalpy grounds. This suggests that the chlorine atom can form a bond using the electrons from the oxygen double bond or from a lone pair on one of the oxygen atoms. Intuitively, we would expect the former neutral to be the accompanying partner in this reaction, as it does not withdraw electron density from the strong double bond. Both hydrogen and fluorine atom removal are also observed with a low branching ratio, although there appears to be some problem with the thermochemical values used to form  $\text{CHCl}_2^+ + \text{FOO}$ . The only way in which this reaction is exothermic is for appreciable vibrational excitation to exist in the  $\text{O}_2^+$  reagent ion. However, as stated in Section 2, the pseudo-first-order kinetic rate graph displays no curvature, so this cannot be the case. The fault for this discrepancy may be the uncertainty in the  $\Delta_f H^\circ_{298}$  value for  $\text{FOO}$ , which has caused many problems for theoretical chemists because of the large number of lone pairs of electrons.<sup>25,26</sup> The  $\text{O}_2^+$  reaction has been studied previously using a selected ion drift tube apparatus,<sup>27</sup> where the measured  $k_{\text{exp}}$  exactly matches our value, but with the branching ratios for the ionic products only broadly agreeing with the data we report; the values they give for  $\text{CHClF}^+$  and  $\text{CCl}_2\text{F}^+$  are 70 and 30%, respectively.



A further inconsistency is evident in the thermochemistry of the reaction involving  $\text{Xe}^+$ , as the two minor channels are only exothermic if the reagent ion is in the higher-energy  $^2\text{P}_{1/2}$  state. The major product channel,  $\text{CHClF}^+$  with a 97% branching ratio, is exothermic when  $\text{Xe}^+$  is in either state. No curvature of any rate plot is observed. Assuming the thermochemistry is correct, we can only conclude that the reactions of  $\text{Xe}^+$  with  $\text{CHCl}_2\text{F}$  to produce  $\text{CCl}_2\text{F}^+$  and  $\text{CHCl}_2^+$  can only proceed from the higher  $^2\text{P}_{1/2}$  spin-orbit state of  $\text{Xe}^+$ . In other words,  $\text{Xe}^+$  is not thermalised under our experimental conditions. By contrast, the reactions of  $\text{Kr}^+$  to produce all three product ions are substantially exothermic from its  $^2\text{P}_{3/2}$  ground state. We should note, however, that reactions of  $\text{Kr}^+$  could also be occurring from both spin-orbit states with identical rate coefficients. The neutral products resulting from the  $\text{N}_2\text{O}^+$  reaction merit discussion, in that forming  $\text{N}_2 + \text{OX}$  as neutral partners is thermochemically more favourable than the more intuitive route to  $\text{N}_2\text{O} + \text{X}$  (where  $\text{X} = \text{Cl}, \text{H}$  or  $\text{F}$ ). The latter set of neutrals might be expected, as they occur from the breaking of one C-X bond, whereas the more enthalpically-favoured route involves cleavage of both the C-X and N=O bonds plus formation of an O-X bond. It is possible, therefore, that either set of neutrals may accompany the detected product ions. Reactions with the  $\text{N}_2^+$  and  $\text{Ar}^+$  ions result in more even distributions of major products, with approximately equal branching ratios between  $\text{CHClF}^+$  and  $\text{CHCl}_2^+$ . At higher recombination energies, greater fragmentation is observed. Both  $\text{CCl}^+$  and  $\text{CF}^+$  are observed as the dominant products from the  $\text{F}^+$  reaction, with formation of  $\text{CHF}^+$  ions taking precedence with  $\text{Ne}^+$ .

In Figure 1, the branching ratios resulting from the threshold photoelectron-photoion coincidence (TPEPICO) work are displayed.<sup>4</sup> Composite ion yields are displayed due to resolution difficulties outlined in the preceding paper.<sup>4</sup> The SIFT branching ratios for ions with recombination energies in the range 12 – 22 eV, corrected so that the sum of the pertinent data equals unity, are overlaid. From this diagram, it is clear that both sets of data agree very well, with the contours for the  $\text{CHClF}^+$  and  $\text{CHCl}_2^+$  ions matching within experimental error. The only discrepancy of note is with the  $\text{F}^+$  data, which overestimates the  $\text{CHClF}^+$  branching ratio with respect to the photoionization results, at the expense of the combined  $\text{CHF}^+/\text{CF}^+$  branching ratio. For a reaction to be considered as proceeding by a pure long-range charge transfer mechanism, the recombination energy of the reagent ion should correspond to an ionisation energy in the neutral reagent where good Franck-Condon factors exist.<sup>3</sup> Such a situation is denoted by an appreciable signal in the threshold photoelectron spectrum (TPES) and the TPES for  $\text{CHCl}_2\text{F}$  is given in Figure 1(a) of the preceding paper.<sup>4</sup> From this information, we can infer that the reactions between  $\text{CHCl}_2\text{F} + \text{O}_2^+$  or  $\text{N}^+$  occur *via* long-range charge transfer, whilst the reactions of the other ions above the ionisation energy of  $\text{CHCl}_2\text{F}$  probably occur by short-range charge transfer, even though the branching ratios match those that would result from the long-range model.

### 3.2.2 CHClF<sub>2</sub>

Table 2 displays the products of the reactions between a variety of cations and CHClF<sub>2</sub>, alongside proposed neutral products and thermochemistry. We initially consider reactions involving ions whose recombination energies are below  $12.15 \pm 0.05$  eV, which is the onset of ionisation for CHClF<sub>2</sub>.<sup>4</sup> Five of the cations used in this study did not react with CHClF<sub>2</sub>, namely H<sub>3</sub>O<sup>+</sup>, SF<sub>3</sub><sup>+</sup>, NO<sup>+</sup>, NO<sub>2</sub><sup>+</sup> and SF<sub>2</sub><sup>+</sup>. The CF<sub>y</sub><sup>+</sup> ions, where  $y = 1, 2$  or  $3$ , display competitive bond cleavage between C-F and C-Cl, with a limited tendency towards hydrogen abstraction. The SF<sub>x</sub><sup>+</sup> ions that do react, however, favour fluorine abstraction exclusively, but all three of these reactions take place non-efficiently ( $k_{\text{exp}} \ll k_{\text{c}}$ ). The reaction with O<sub>2</sub><sup>+</sup> displays the same thermochemical limitations as described in Section 3.2.1, with the additional uncertainty in the heats of formation of ClOO and OClO. The thermochemistry suggests that the  $v \geq 1$  level of the reagent ion reacts to form CHF<sub>2</sub><sup>+</sup>, although an absence of curvature in the pseudo-first-order rate plot makes this possibility difficult to prove. As only one fifth of the population of O<sub>2</sub><sup>+</sup> is in its higher vibrational levels,<sup>10</sup> and yet they yield the major ionic product with a 70% branching ratio, this cannot be a satisfactory explanation for the observed phenomenon. In addition to the thermochemical issues regarding the neutral species, we note that the value quoted for CHF<sub>2</sub><sup>+</sup>,  $+604$  kJ mol<sup>-1</sup>, is an upper limit to  $\Delta_f H^\circ_{298}$ .<sup>28</sup> Another study of this reaction using a selected ion drift tube gave an inverted product distribution, with CClF<sub>2</sub><sup>+</sup> and CHF<sub>2</sub><sup>+</sup> having branching ratios of 74 and 26%, respectively.<sup>27</sup> Additionally,  $k_{\text{exp}}$  is given as  $0.85 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>, which is less than half the MADO capture value calculated by us. We cannot explain why this study appears to give concurrent results for the O<sub>2</sub><sup>+</sup> + CHCl<sub>2</sub>F reaction, but significantly different results for O<sub>2</sub><sup>+</sup> + CHClF<sub>2</sub>. The results for the reaction with Xe<sup>+</sup> show the same inconsistency as described in Section 3.2.1, in that the thermochemistry points towards reaction only occurring with the <sup>2</sup>P<sub>1/2</sub> excited state. The observed straight line rate graph demonstrates that both spin-orbit states react at the same rate, or that the <sup>2</sup>P<sub>3/2</sub> level has insufficient energy to react. This effect is now also true for the major product channel, CHF<sub>2</sub><sup>+</sup> with 94% branching ratio.

At recombination energies between 12.15 and 14.53 eV, CHF<sub>2</sub><sup>+</sup> production is by far the most dominant route, with its branching ratio not falling below 76% over this energy range. The reaction with N<sub>2</sub>O<sup>+</sup> that forms CHClF<sup>+</sup> at the 3% level does not have the option to produce N<sub>2</sub>O + F as the accompanying neutrals, unlike the major product channel producing N<sub>2</sub>O + Cl, due to the inherent endothermicity,  $+60$  kJ mol<sup>-1</sup>, of producing these neutrals. Therefore, the near thermoneutral reaction forming CHClF<sup>+</sup> + N<sub>2</sub> + OF is the only accessible pathway. At even higher energy, the major product formed from the reactions involving N<sub>2</sub><sup>+</sup>, Ar<sup>+</sup> and F<sup>+</sup> is CHClF<sup>+</sup> produced at the *ca.* 65% level. Appreciable formation of CHF<sub>2</sub><sup>+</sup> still occurs in reactions with the former two ions, although with F<sup>+</sup> the emergence of smaller ions such as CF<sup>+</sup> is evident. This trend is extended further in the reaction involving Ne<sup>+</sup>, where the major product is Cl<sup>+</sup>, an atomic ion. A range of other product ions is also observed, although not the parent ion. The composite breakdown diagram resulting from the photoionization from CHClF<sub>2</sub> using the TPEPICO

technique,<sup>4</sup> alongside the corrected SIFT branching ratios, is shown in Figure 2. Reasonable agreement exists between the two sets of data, although the data for  $\text{Ne}^+$  appears to show a reversal in the branching ratios for  $\text{CF}^+/\text{CHF}^+$  and  $\text{CF}_2^+/\text{CHF}_2^+$  and a vastly increased yield of  $\text{CHClF}^+$ . From the TPES for this molecule (Figure 3(a) in the preceding paper),<sup>4</sup> it can be demonstrated that only the reactions of  $\text{CHClF}_2$  with  $\text{N}_2\text{O}^+$ ,  $\text{Kr}^+$ ,  $\text{CO}^+$ ,  $\text{N}_2^+$  and  $\text{Ar}^+$  appear to have sufficient Franck-Condon overlap to occur *via* the long-range charge transfer mechanism. Any other results that resemble the TPEPICO data are assumed to fit the short-range model, even though the products match those expected from the long-range model.

### 3.2.3 $\text{CH}_2\text{ClF}$

The ionic and proposed neutral products of reaction between atomic and molecular ions with  $\text{CH}_2\text{ClF}$  are listed in Table 3. Below the onset of ionisation of  $\text{CH}_2\text{ClF}$ , determined as  $11.63 \pm 0.05$  eV,<sup>4</sup> only  $\text{CF}_y^+$ , where  $y = 1, 2$  or  $3$ ,  $\text{SF}_5^+$  and  $\text{SF}^+$  react at an observable rate. The  $\text{CF}_y^+$  species show a preference for fluorine atom removal, with the subsequent ion  $\text{CH}_2\text{Cl}^+$  being the most dominant product with a branching ratio of *ca.* 90%. The  $\text{CF}_3^+$  reaction has been studied previously using an ion cyclotron resonance mass spectrometer (ICR-MS), but the results are very different.<sup>29</sup> In this earlier study,  $\text{CH}_2\text{F}^+$  was the major product (95%) together with only 5% of  $\text{CH}_2\text{Cl}^+$ , and the reaction proceeds with a much lower rate coefficient. These observations may be explained by the formation of a longer-lived transition state than is indicated by our efficient reaction.<sup>30</sup> Additionally, the operating pressure inside an ICR-MS is much lower than that inside a SIFT, resulting in non-thermalised reagents and different product distributions. As an extension of the aforementioned  $\text{CF}_y^+$  trend, the  $\text{SF}_5^+$  reaction proceeds *via* C-F bond cleavage to form  $\text{CH}_2\text{Cl}^+$ , now with a yield of 100%. This may be due to the stabilisation that formation of  $\text{SF}_6$  conveys. Competition between Cl and H atom removal is observed in the  $\text{SF}^+$  reaction, as the respective resultant ionic products have approximately the same branching ratio. The heats of formation for the suggested neutrals  $\text{SClF}$  and  $\text{SHF}$  have not been established, but these reactions would occur spontaneously if the  $\Delta_f H^\circ_{298}$  for these two molecules were less than  $-97$  and  $-7$   $\text{kJ mol}^{-1}$ , respectively. As the heats of formation at 298 K for  $\text{SCl}_2$ ,  $\text{SH}_2$  and  $\text{SF}_2$  are  $-18$ ,  $-21$  and  $-295$   $\text{kJ mol}^{-1}$ , respectively, these suggestions seem plausible.<sup>22,23</sup>

Above the onset of ionisation of  $\text{CH}_2\text{ClF}$  there is the opportunity for long-range charge transfer to happen. Interestingly,  $\text{SF}_4^+$  reacts to give solely  $\text{CH}_2\text{Cl}^+$ . As for the  $\text{SF}_5^+$  reaction, a possible explanation is the formation of the comparatively stable  $\text{SF}_5$  species, with  $\Delta_f H^\circ_{298} = -915$   $\text{kJ mol}^{-1}$ . From 12.07 ( $\text{O}_2^+$ ) to 12.89 eV ( $\text{N}_2\text{O}^+$ ), the major product is the parent ion. There is also an appreciable amount of  $\text{CHClF}^+$  detected over this range. The uncertainty in the thermochemistry of the FOO radical may explain the production of  $\text{CH}_2\text{Cl}^+$  at 8% from  $\text{O}_2^+ + \text{CH}_2\text{ClF}$ , despite  $\nu^+ = 0 - 2$  of  $\text{O}_2^+$  being endothermic reactions. The reactions of  $\text{Xe}^+$  once again display the inconsistencies described in detail for  $\text{CHCl}_2\text{F}$  in section 3.2.1, and the arguments are not repeated here. Neither the  $\text{O}_2^+$  or  $\text{Xe}^+$  reaction displays any curvature in

their respective rate plots. It is worth noting that the major product of the  $\text{Xe}^+$  reaction may be formed from either spin-orbit state of the reagent ion, and that the parent ion formed by  $\text{N}_2\text{O}^+$  can only be formed with  $\text{N}_2\text{O}$  as the neutral partner. This is the only time this molecule is a preferred neutral product in any of the  $\text{N}_2\text{O}^+$  reactions studied here. Within the energy range 13.62 – 15.76 eV,  $\text{CH}_2\text{F}^+$  is the dominant product, with a branching ratio between 55 and 93%. Varying amounts of  $\text{CH}_2\text{Cl}^+$ ,  $\text{CHClF}^+$  and the parent ion are observed from all the reactions in this range. The  $\text{F}^+$  reaction strongly favours  $\text{CH}_2\text{Cl}^+$  formation, possibly because  $\text{F}_2$  is a stable neutral partner. The reaction with  $\text{Ne}^+$  forms a multitude of smaller ions, with  $\text{CHF}^+$  figuring prominently. The  $\text{CF}^+$  product can be formed with either  $\text{H}_2 + \text{Cl} + \text{Ne}$  or  $\text{HCl} + \text{H} + \text{Ne}$ , as both of these reactions are approximately isoenthalpic. With reference to Figure 3, which depicts the breakdown diagram from the TPEPICO experiment<sup>4</sup> and the corrected branching ratios from this work, it is clear that the fit between the two data sets is not as close as for the other two molecules. Anomalies include reactions with  $\text{SF}_4^+$  where completely different products are observed, and  $\text{N}_2^+$ ,  $\text{Ar}^+$  and  $\text{Ne}^+$  where an increase in one product is offset with a decrease in another. Using the intensities of peaks in the TPES of  $\text{CH}_2\text{ClF}$  (Figure 4(a) in the preceding paper) as a guide to Franck-Condon factors, it can be concluded that the reactions of  $\text{Kr}^+$ ,  $\text{CO}^+$  and  $\text{N}^+$  occur *via* long-range charge transfer. All other reactions occur by other mechanisms, even if the products match those of the long-range model.

#### 4. Conclusions

The branching ratios and rate coefficients have been measured at 298 K for the reactions between  $\text{CHCl}_2\text{F}$ ,  $\text{CHClF}_2$  and  $\text{CH}_2\text{ClF}$  and the following cations;  $\text{H}_3\text{O}^+$ ,  $\text{SF}_x^+$  (where  $x = 1, 2, 3, 4$  or  $5$ ),  $\text{CF}_y^+$  (where  $y = 1, 2$  or  $3$ ),  $\text{NO}^+$ ,  $\text{NO}_2^+$ ,  $\text{O}_2^+$ ,  $\text{Xe}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{Kr}^+$ ,  $\text{CO}^+$ ,  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{F}^+$  and  $\text{Ne}^+$ . Comparisons between experimental and calculated rate coefficients indicate that the vast majority of reactions occur efficiently. No reactions are observed between any of the neutrals and  $\text{SF}_3^+$ ,  $\text{NO}^+$ ,  $\text{NO}_2^+$  and  $\text{SF}_2^+$ . This is attributed to the endothermic nature of all the available reaction processes. The  $\text{H}_3\text{O}^+$  ion only reacts with  $\text{CHCl}_2\text{F}$ , even though all of the observed channels are apparently endothermic. Attempts to rationalise this observation using entropic effects and incorrect thermochemistry fall short of a plausible explanation. The  $\text{CF}_y^+$  series all react *via* single bond dissociation of the neutral in the collision complex to form a single neutral halocarbon species. All of the reagent ions in the  $\text{SF}_x^+$  series react inefficiently with  $\text{CHClF}_2$  forming  $\text{CHClF}^+$  as the sole ionic product, implying that fluorine-atom transfer is hindered in these complexes. The reactions involving  $\text{O}_2^+$  demonstrate that the  $\Delta_f H^\circ_{298}$  for FOO is not established, in agreement with recent theoretical work.<sup>25,26</sup>  $\text{Xe}^+$  appears to react either when it is only in its higher-energy  $^2\text{P}_{1/2}$  spin-orbit state or when both spin-orbit states react with the same rate coefficient. This result appears to contradict previous data from our SIFT apparatus involving  $\text{Xe}^+$ , where different rates were observed for each spin-orbit state, with the  $^2\text{P}_{3/2}$  state reacting significantly faster.<sup>13</sup> We can only conclude that the operating conditions of the ion source and flow tube were different in these

two studies. From a thermochemical perspective, the reactions of  $\text{N}_2\text{O}^+$  may proceed *via* charge transfer with dissociation in both the reagent cation and neutral, although extensive rearrangements are required. Chlorine-atom abstraction is favoured for reactions with  $\text{Xe}^+$ ,  $\text{N}_2\text{O}^+$ ,  $\text{O}^+$ ,  $\text{CO}_2^+$ ,  $\text{Kr}^+$ ,  $\text{CO}^+$  and  $\text{N}^+$  ions, except in the case of the first two ions with  $\text{CH}_2\text{ClF}$ . This favourable trend can be justified using the relative bond strengths available in the neutral molecules, where C-Cl is clearly the weakest bond.<sup>4,32</sup> This is further supported by the Cl lone pair and C-Cl  $\sigma$ -bonding orbital character evident in all three neutrals over the energy region that corresponds to the recombination energies of these reagent ions.<sup>4</sup> It is interesting to note that the product branching ratios resulting from reactions with atomic and molecular ions that possess virtually identical recombination energy are exceedingly similar, as demonstrated by the  $\text{Kr}^+$  and  $\text{CO}^+$  data. Equivalent results are noted when comparing the  $\text{N}_2^+$  and  $\text{Ar}^+$  results, where competition between chlorine or fluorine removal exists. As expected, increased fragmentation is noted at the highest recombination energies, with  $\text{Cl}^+$ ,  $\text{CF}^+$  and  $\text{CHF}^+$  products figuring prominently. Upper limits for  $\Delta_f H^\circ_{298}$ , where values could not be sourced from the literature, can be useful guides to thermochemistry. These are derived for the molecules  $\text{SClF}$ ,  $\text{SF}_4\text{Cl}$  and  $\text{SHF}$  as  $-28$ ,  $-637$  and  $-7$   $\text{kJ mol}^{-1}$ . The value for  $\text{SClF}$  is taken from the reaction between  $\text{SF}^+$  and  $\text{CHCl}_2\text{F}$ , rather than with  $\text{CH}_2\text{ClF}$ , as the former gives a higher branching ratio for  $\text{SClF}$  production.

Genuine long-range charge transfer, where substantial overlap between the ground state and an accessible ionic state in the neutral molecule exists at the recombination energy of the reagent ion plus an agreement between TPEPICO and SIFT branching ratios,<sup>3</sup> is observed in about ten out of a total of fifty-five reactions studied. The only results which notably conflict with those of the TPEPICO study, rather than display systematic differences, are the  $\text{F}^+ + \text{CHCl}_2\text{F}$ ,  $\text{Ne}^+ + \text{CHClF}_2$  and, to a lesser extent,  $\text{Ne}^+ + \text{CH}_2\text{ClF}$ . These three reactions take place at recombination energies that coincide with the lowest intensity on the relevant TPES, thereby emphasising the importance of the Franck-Condon overlap on the accord between the two sets of results. Generally, the results for  $\text{CHCl}_2\text{F}$  and  $\text{CHClF}_2$ , where dissociative charge transfer dominates and parent ion signal is rarely seen in major abundance, are similar to those found in the recent SIFT studies performed on the analogous  $\text{CHBr}_2\text{F}$  and  $\text{CHBrF}_2$  molecules, respectively.<sup>5</sup> The profile of the product ion signal variation as a function of neutral reagent for each individual reaction indicates which secondary processes are occurring at higher neutral gas flow. The vast majority of these graphs for  $\text{CHCl}_2\text{F}$  and  $\text{CHClF}_2$  mimic those obtained using a high-pressure mass spectrometer,<sup>33</sup> in that  $\text{CHClF}^+$  reacts on to form  $\text{CHCl}_2^+$  in the former case and  $\text{CHF}_2^+$  produces  $\text{CHClF}^+$  at high flows of the neutral reactant. The only exceptions to this consensus are those plots derived from reactions involving ions with high recombination energies, where the presence of more fragmented products complicates this matter. However, derivative processes such as these only warrant a cursory mention, as the branching ratios derived from extrapolation to zero flow of the neutral gas are the prime focus of this study. The  $\text{CH}_2\text{ClF}$  results fall into a separate group to the other two molecules of interest to this work, as non-dissociative

charge transfer is evident in increased levels and even dominates in some cases. These findings concur with the recent work performed on CH<sub>2</sub>BrF and CH<sub>2</sub>BrCl.<sup>5</sup>

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**Table 1** Rate coefficients at 298 K, product cations, branching ratios, and suggested neutral products for the reactions of twenty-three cations with CHCl<sub>2</sub>F. The recombination energy (RE) of the ion is shown in column 1. Experimental rate coefficients are shown in column 2; values in square brackets below the experimental data are MADO theoretical capture coefficients (see text). The product ions and their branching ratios are shown in column 3. The most likely accompanying neutral products are given in column 4, with the enthalpy of the proposed reaction given in column 5. These values are generally derived from the usual reference sources for neutrals<sup>22</sup> and ions,<sup>34</sup> unless otherwise indicated. In the interests of brevity, only the proposed neutrals that give the most exothermic  $\Delta_r H^\circ_{298}$  are listed, unless specifically discussed in Sections 3 or 4.

Reagent ion (RE / eV)	Rate coefficient / $10^{-9} \text{ cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	Product ions (%)	Proposed neutral products	$\Delta_r H^\circ_{298} / \text{kJ mol}^{-1}$
H <sub>3</sub> O <sup>+</sup> (6.27)	1.6 [2.2]	CCl <sub>2</sub> F <sup>+</sup> (85) CHCl <sub>2</sub> <sup>+</sup> (11) CHClF <sup>+</sup> (4)	H <sub>2</sub> O + H <sub>2</sub> H <sub>2</sub> O + HF H <sub>2</sub> O + HCl	+154 +65 +101
SF <sub>3</sub> <sup>+</sup> (8.26)	[1.3]	No reaction		
CF <sub>3</sub> <sup>+</sup> (9.03)	1.3 [1.4]	CHClF <sup>+</sup> (83) CHCl <sub>2</sub> <sup>+</sup> (17)	CClF <sub>3</sub> CF <sub>4</sub>	-88 <sup>a</sup> -169 <sup>a</sup>
CF <sup>+</sup> (9.10)	1.6 [1.8]	CHClF <sup>+</sup> (71) CHCl <sub>2</sub> <sup>+</sup> (29) CCl <sub>2</sub> F <sup>+</sup> (trace)	CClF CF <sub>2</sub> CHF	-77 <sup>b</sup> -146 -5 <sup>c</sup>
NO <sup>+</sup> (9.26)	[1.8]	No reaction		
SF <sub>5</sub> <sup>+</sup> (9.55)	0.4 [1.2]	CHClF <sup>+</sup> (73) CHCl <sub>2</sub> <sup>+</sup> (27)	SF <sub>5</sub> Cl SF <sub>6</sub>	-42 <sup>d</sup> -79 <sup>d</sup>
NO <sub>2</sub> <sup>+</sup> (9.59)	[1.6]	No reaction		
SF <sub>2</sub> <sup>+</sup> (10.17)	[1.4]	No reaction		
SF <sup>+</sup> (10.25)	1.5 [1.5]	CHClF <sup>+</sup> (92) CHCl <sub>2</sub> <sup>+</sup> (8)	SClF SF <sub>2</sub>	+28 + $\Delta_r H^\circ_{298}(\text{SClF})$ <sup>e</sup> -123 <sup>e,f</sup>
CF <sub>2</sub> <sup>+</sup> (11.43)	1.2 [1.5]	CHClF <sup>+</sup> (61) CHCl <sub>2</sub> <sup>+</sup> (39) CCl <sub>2</sub> F <sup>+</sup> (trace)	CClF <sub>2</sub> CF <sub>3</sub> CHF <sub>2</sub>	-175 <sup>g,h</sup> -218 <sup>g,i</sup> -173 <sup>g</sup>
SF <sub>4</sub> <sup>+</sup> (11.92)	0.9 [1.2]	CHClF <sup>+</sup> (100)	SF <sub>4</sub> Cl or SF <sub>4</sub> + Cl	+637 + $\Delta_r H^\circ_{298}(\text{SF}_4\text{Cl})$ <sup>j</sup> or -10 <sup>j,k</sup>
O <sub>2</sub> <sup>+</sup> (12.07)	1.9 [1.8]	CHClF <sup>+</sup> (94) CCl <sub>2</sub> F <sup>+</sup> (5) CHCl <sub>2</sub> <sup>+</sup> (1)	ClOO or OCIO HOO FOO	-40 or -41 -176 +31, +9, -13 <sup>l</sup>
Xe <sup>+</sup> (12.13/13.44) <sup>m</sup>	1.2 [1.2]	CHClF <sup>+</sup> (97) CCl <sub>2</sub> F <sup>+</sup> (3) CHCl <sub>2</sub> <sup>+</sup> (trace)	Xe + Cl Xe + H Xe + F	-23, -149 <sup>m</sup> +34, -92 <sup>m</sup> +79, -47 <sup>m</sup>
N <sub>2</sub> O <sup>+</sup> (12.89)	1.1 [1.6]	CHClF <sup>+</sup> (95) CCl <sub>2</sub> F <sup>+</sup> (3) CHCl <sub>2</sub> <sup>+</sup> (2)	N <sub>2</sub> + OCl or N <sub>2</sub> O + Cl N <sub>2</sub> + OH or N <sub>2</sub> O + H N <sub>2</sub> + OF or N <sub>2</sub> O + F	-198 or -96 -301 or -40 -47 or +6



O <sup>+</sup> (13.62)	1.8 [2.4]	CHClF <sup>+</sup> (95) CHCl <sub>2</sub> <sup>+</sup> (5) CCl <sub>2</sub> F <sup>+</sup> (trace)	OCl OF OH	-435 -284 -538
CO <sub>2</sub> <sup>+</sup> (13.78)	1.4 [1.6]	CHClF <sup>+</sup> (99) CCl <sub>2</sub> F <sup>+</sup> (1) CHCl <sub>2</sub> <sup>+</sup> (trace)	CO <sub>2</sub> + Cl CO <sub>2</sub> + H CO <sub>2</sub> + F	-181 -124 -79
Kr <sup>+</sup> (14.00)	1.0 [1.3]	CHClF <sup>+</sup> (94) CHCl <sub>2</sub> <sup>+</sup> (3) CCl <sub>2</sub> F <sup>+</sup> (3)	Kr + Cl Kr + F Kr + H	-203 -101 -147
CO <sup>+</sup> (14.01)	1.7 [1.9]	CHClF <sup>+</sup> (95) CHCl <sub>2</sub> <sup>+</sup> (3) CCl <sub>2</sub> F <sup>+</sup> (2)	COCl COF COH	-278 -242 -211
N <sup>+</sup> (14.53)	2.5 [2.5]	CHClF <sup>+</sup> (92) CHCl <sub>2</sub> <sup>+</sup> (6) CCl <sub>2</sub> F <sup>+</sup> (2)	NCl NF NH	-535 <sup>n</sup> -456 -512
N <sub>2</sub> <sup>+</sup> (15.58)	1.6 [1.9]	CHClF <sup>+</sup> (50) CHCl <sub>2</sub> <sup>+</sup> (45) CCl <sub>2</sub> F <sup>+</sup> (5)	N <sub>2</sub> + Cl N <sub>2</sub> + F N <sub>2</sub> + H	-355 -253 -299
Ar <sup>+</sup> (15.76)	1.3 [1.7]	CHCl <sub>2</sub> <sup>+</sup> (46) CHClF <sup>+</sup> (43) CCl <sub>2</sub> F <sup>+</sup> (6) CF <sup>+</sup> (5)	Ar + F Ar + Cl Ar + H Ar + HCl + Cl	-271 -373 -317 -75
F <sup>+</sup> (17.42)	2.0 [2.2]	CCl <sub>2</sub> <sup>+</sup> (48) CF <sup>+</sup> (26) CHClF <sup>+</sup> (21) CHCl <sub>2</sub> <sup>+</sup> (5) CCl <sub>2</sub> F <sup>+</sup> (trace)	HF + ClF HF + Cl <sub>2</sub> ClF F <sub>2</sub> HF	-557 -615 -784 -590 -1046
Ne <sup>+</sup> (21.56)	1.9 [2.2]	CHF <sup>+</sup> (43) CF <sup>+</sup> (15) CHCl <sup>+</sup> (15) CHClF <sup>+</sup> (11) Cl <sup>+</sup> (8) CHCl <sub>2</sub> <sup>+</sup> (4) CCl <sub>2</sub> <sup>+</sup> (4) CClF <sup>+</sup> (trace) CCl <sub>2</sub> <sup>+</sup> (trace) CCl <sub>2</sub> F <sup>+</sup> (trace) CHCl <sub>2</sub> F <sup>+</sup> (trace)	Ne + Cl <sub>2</sub> Ne + HCl + Cl Ne + ClF Ne + Cl Ne + CHClF Ne + F Ne + HF + Cl Ne + HCl Ne + HF Ne + H Ne	-676 -634 -600 -932 -531 -830 -705 -872 -906 -876 -968

<sup>a</sup>  $\Delta_f H^\circ_{298}(\text{CF}_3^+) = +406 \text{ kJ mol}^{-1}$ .<sup>35</sup> <sup>b</sup>  $\Delta_f H^\circ_{298}(\text{CClF}) = +31 \text{ kJ mol}^{-1}$ .<sup>36</sup> <sup>c</sup>  $\Delta_f H^\circ_{298}(\text{CHF}) = +143 \text{ kJ mol}^{-1}$ .<sup>36</sup> <sup>d</sup>  $\Delta_f H^\circ_{298}(\text{SF}_5^+) = +29 \text{ kJ mol}^{-1}$ .<sup>37</sup> <sup>e</sup>  $\Delta_f H^\circ_{298}(\text{SF}^+) = +998 \text{ kJ mol}^{-1}$ .<sup>23</sup> <sup>f</sup>  $\Delta_f H^\circ_{298}(\text{SF}_2) = -295 \text{ kJ mol}^{-1}$ .<sup>23</sup> <sup>g</sup>  $\Delta_f H^\circ_{298}(\text{CF}_2^+) = +922 \text{ kJ mol}^{-1}$ , calculated from  $\Delta_f H^\circ_{298}(\text{CF}_2) + \text{IE}(\text{CF}_2)$ .<sup>21</sup> <sup>h</sup>  $\Delta_f H^\circ_{298}(\text{CClF}_2) = -279 \text{ kJ mol}^{-1}$ .<sup>38</sup> <sup>i</sup>  $\Delta_f H^\circ_{298}(\text{CF}_3) = -466 \text{ kJ mol}^{-1}$ .<sup>34</sup> <sup>j</sup>  $\Delta_f H^\circ_{298}(\text{SF}_4^+) = +389 \text{ kJ mol}^{-1}$ .<sup>23</sup> <sup>k</sup>  $\Delta_f H^\circ_{298}(\text{SF}_4) = -768 \text{ kJ mol}^{-1}$ .<sup>23</sup> <sup>l</sup> The three values quoted are for the enthalpy of reaction at 298 K involving the  $\nu = 0, 1,$  and  $2$  levels of the ground electronic state of  $\text{O}_2^+$ , using  $\text{O}_2^+$  ground state vibrational spectroscopic constants.<sup>21</sup> <sup>m</sup> The two values quoted are for the enthalpy of reaction at 298 K involving the  $^2\text{P}_{3/2}$  and  $^2\text{P}_{1/2}$  spin-orbit states of  $\text{Xe}^+$ .<sup>12</sup> <sup>n</sup>  $\Delta_f H^\circ_{298}(\text{NCl}) = +314 \text{ kJ mol}^{-1}$ .<sup>39</sup>

**Table 2** Rate coefficients at 298 K, product cations, branching ratios, and suggested neutral products for the reactions of twenty-three cations with  $\text{CHClF}_2$ . The recombination energy (RE) of the ion is shown in column 1. Experimental rate coefficients are shown in column 2; values in square brackets below the experimental data are MADDO theoretical capture coefficients (see text). The product ions and their branching ratios are shown in column 3. The most likely accompanying neutral products are given in column 4, with the enthalpy of the proposed reaction given in column 5. These values are generally derived from the usual reference sources for neutrals<sup>22</sup> and ions,<sup>34</sup> unless otherwise indicated. In the interests of brevity, only the proposed neutrals that give the most exothermic  $\Delta_r H^\circ_{298}$  are listed, unless specifically discussed in Sections 3 or 4.

Reagent ion (RE / eV)	Rate coefficient $/ 10^{-9} \text{ cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	Product ions (%)	Proposed neutral products	$\Delta_r H^\circ_{298} / \text{kJ mol}^{-1}$
$\text{H}_3\text{O}^+$ (6.27)	[2.3]	No reaction		
$\text{SF}_3^+$ (8.26)	[1.4]	No reaction		
$\text{CF}_3^+$ (9.03)	1.0 [1.5]	$\text{CHF}_2^+$ (55) $\text{CHClF}^+$ (40) $\text{CClF}_2^+$ (5)	$\text{CF}_3\text{Cl}$ $\text{CF}_4$ $\text{CHF}_3$	-28 <sup>a,b</sup> -115 <sup>a</sup> -93 <sup>a</sup>
$\text{CF}^+$ (9.10)	2.0 [1.9]	$\text{CHClF}^+$ (85) $\text{CHF}_2^+$ (15) $\text{CClF}_2^+$ (trace)	$\text{CF}_2$ $\text{CClF}$ $\text{CHF}$	-91 -17 <sup>b,c</sup> +19 <sup>d</sup>
$\text{NO}^+$ (9.26)	[1.9]	No reaction		
$\text{SF}_5^+$ (9.55)	0.8 [1.3]	$\text{CHClF}^+$ (100)	$\text{SF}_6$	-25 <sup>e</sup>
$\text{NO}_2^+$ (9.59)	[1.7]	No reaction		
$\text{SF}_2^+$ (10.17)	[1.5]	No reaction		
$\text{SF}^+$ (10.25)	0.5 [1.6]	$\text{CHClF}^+$ (100)	$\text{SF}_2$	-69 <sup>f,g</sup>
$\text{CF}_2^+$ (11.43)	1.7 [1.6]	$\text{CHClF}^+$ (59) $\text{CHF}_2^+$ (30) $\text{CClF}_2^+$ (11)	$\text{CF}_3$ $\text{CClF}_2$ $\text{CHF}_2$	-163 <sup>h,i</sup> -115 <sup>b,h,j</sup> -149 <sup>h</sup>
$\text{SF}_4^+$ (11.92)	0.6 [1.3]	$\text{CHClF}^+$ (100)	$\text{SF}_5$	-80 <sup>k,l</sup>
$\text{O}_2^+$ (12.07)	1.7 [1.9]	$\text{CHF}_2^+$ (70) $\text{CHClF}^+$ (25) $\text{CClF}_2^+$ (5)	$\text{ClOO}$ or $\text{OCIO}$ $\text{FOO}$ $\text{HOO}$	+19, -3, -25 <sup>b,m</sup> +18, -4, -26 <sup>m</sup> +85, +63, +41 <sup>m</sup> -153
$\text{Xe}^+$ (12.13/13.44) <sup>n</sup>	1.3 [1.3]	$\text{CHF}_2^+$ (94) $\text{CHClF}^+$ (6) $\text{CClF}_2^+$ (trace) $\text{CHClF}_2^+$ (trace)	$\text{Xe} + \text{Cl}$ $\text{Xe} + \text{F}$ $\text{Xe} + \text{H}$ $\text{Xe}$	+36, -90 <sup>b,n</sup> +134, +7 <sup>n</sup> +57, -69 <sup>n</sup> +5, -121 <sup>n</sup>
$\text{N}_2\text{O}^+$ (12.89)	1.5 [1.7]	$\text{CHF}_2^+$ (97) $\text{CHClF}^+$ (3)	$\text{N}_2 + \text{OCl}$ or $\text{N}_2\text{O} + \text{Cl}$ $\text{N}_2 + \text{OF}$ or $\text{N}_2\text{O} + \text{F}$	-139 <sup>b</sup> or -37 <sup>b</sup> +8 or +60
$\text{O}^+$	2.4	$\text{CHF}_2^+$ (86)	$\text{OCl}$	-376 <sup>b</sup>

(13.62)	[2.5]	CHClF <sup>+</sup> (14)	OF	-229
CO <sub>2</sub> <sup>+</sup> (13.78)	1.5 [1.7]	CHF <sub>2</sub> <sup>+</sup> (94) CHClF <sup>+</sup> (6)	CO <sub>2</sub> + Cl CO <sub>2</sub> + F	-122 <sup>b</sup> -25
Kr <sup>+</sup> (14.00)	1.3 [1.4]	CHF <sub>2</sub> <sup>+</sup> (76) CHClF <sup>+</sup> (24)	Kr + Cl Kr + F	-144 <sup>b</sup> -47
CO <sup>+</sup> (14.01)	2.0 [2.0]	CHF <sub>2</sub> <sup>+</sup> (88) CHClF <sup>+</sup> (12)	COCl COF	-218 <sup>b</sup> -188
N <sup>+</sup> (14.53)	2.7 [2.6]	CHF <sub>2</sub> <sup>+</sup> (84) CHClF <sup>+</sup> (16)	NCl NF	-476 <sup>b,o</sup> -402
N <sub>2</sub> <sup>+</sup> (15.58)	2.0 [2.0]	CHClF <sup>+</sup> (63) CHF <sub>2</sub> <sup>+</sup> (37) CHClF <sub>2</sub> <sup>+</sup> (trace)	N <sub>2</sub> + F N <sub>2</sub> + Cl N <sub>2</sub>	-199 -296 <sup>b</sup> -327
Ar <sup>+</sup> (15.76)	1.7 [1.7]	CHClF <sup>+</sup> (69) CHF <sub>2</sub> <sup>+</sup> (31) CHClF <sub>2</sub> <sup>+</sup> (trace)	Ar + F Ar + Cl Ar	-217 -314 <sup>b</sup> -345
F <sup>+</sup> (17.42)	2.1 [2.3]	CHClF <sup>+</sup> (69) CF <sup>+</sup> (25) CHF <sub>2</sub> <sup>+</sup> (5) CHClF <sub>2</sub> <sup>+</sup> (1)	F <sub>2</sub> HF + ClF ClF F	-535 -467 -725 <sup>b</sup> -505
Ne <sup>+</sup> (21.56)	1.7 [2.3]	Cl <sup>+</sup> (27) CHF <sub>2</sub> <sup>+</sup> (25) CHF <sup>+</sup> (14) CHClF <sup>+</sup> (14) CF <sub>2</sub> <sup>+</sup> (12) CF <sup>+</sup> (7) CClF <sub>2</sub> <sup>+</sup> (1)	Ne + CHF <sub>2</sub> Ne + Cl Ne + ClF Ne + F Ne + HCl Ne + HF + Cl Ne + H	-465 -873 <sup>b</sup> -528 -776 -769 <sup>h</sup> -616 -852

<sup>a</sup>  $\Delta_f H^\circ_{298}(\text{CF}_3^+) = +406 \text{ kJ mol}^{-1}$ .<sup>35</sup> <sup>b</sup>  $\Delta_f H^\circ_{298}(\text{CHF}_2^+) = +604 \text{ kJ mol}^{-1}$ .<sup>28</sup> <sup>c</sup>  $\Delta_f H^\circ_{298}(\text{CClF}) = +31 \text{ kJ mol}^{-1}$ .<sup>36</sup> <sup>d</sup>  $\Delta_f H^\circ_{298}(\text{CHF}) = +143 \text{ kJ mol}^{-1}$ .<sup>36</sup> <sup>e</sup>  $\Delta_f H^\circ_{298}(\text{SF}_5^+) = +29 \text{ kJ mol}^{-1}$ .<sup>37</sup> <sup>f</sup>  $\Delta_f H^\circ_{298}(\text{SF}^+) = +998 \text{ kJ mol}^{-1}$ .<sup>23</sup> <sup>g</sup>  $\Delta_f H^\circ_{298}(\text{SF}_2) = -295 \text{ kJ mol}^{-1}$ .<sup>23</sup> <sup>h</sup>  $\Delta_f H^\circ_{298}(\text{CF}_2^+) = +922 \text{ kJ mol}^{-1}$ , calculated from  $\Delta_f H^\circ_{298}(\text{CF}_2) + \text{IE}(\text{CF}_2)$ .<sup>21</sup> <sup>i</sup>  $\Delta_f H^\circ_{298}(\text{CF}_3) = -466 \text{ kJ mol}^{-1}$ .<sup>35</sup> <sup>j</sup>  $\Delta_f H^\circ_{298}(\text{CClF}_2) = -279 \text{ kJ mol}^{-1}$ .<sup>38</sup> <sup>k</sup>  $\Delta_f H^\circ_{298}(\text{SF}_4^+) = +389 \text{ kJ mol}^{-1}$ .<sup>23</sup> <sup>l</sup>  $\Delta_f H^\circ_{298}(\text{SF}_5) = -915 \text{ kJ mol}^{-1}$ .<sup>40</sup> <sup>m</sup> The three values quoted are for the enthalpy of reaction at 298 K involving the  $\nu = 0, 1,$  and  $2$  levels of the ground electronic state of  $\text{O}_2^+$ , using  $\text{O}_2^+$  ground state vibrational spectroscopic constants.<sup>21</sup> <sup>n</sup> The two values quoted are for the enthalpy of reaction at 298 K involving the  $^2\text{P}_{3/2}$  and  $^2\text{P}_{1/2}$  spin-orbit states of  $\text{Xe}^+$ .<sup>12</sup> <sup>o</sup>  $\Delta_f H^\circ_{298}(\text{NCl}) = +314 \text{ kJ mol}^{-1}$ .<sup>39</sup>

**Table 3** Rate coefficients at 298 K, product cations, branching ratios, and suggested neutral products for the reactions of twenty-three cations with CH<sub>2</sub>ClF. The recombination energy (RE) of the ion is shown in column 1. Experimental rate coefficients are shown in column 2; values in square brackets below the experimental data are MADDO theoretical capture coefficients (see text). The product ions and their branching ratios are shown in column 3. The most likely accompanying neutral products are given in column 4, with the enthalpy of the proposed reaction given in column 5. These values are generally derived from the usual reference sources for neutrals<sup>22</sup> and ions,<sup>34</sup> unless otherwise indicated. In the interests of brevity, only the proposed neutrals that give the most exothermic  $\Delta_r H^\circ_{298}$  are listed, unless specifically discussed in Sections 3 or 4.

Reagent ion (RE / eV)	Rate coefficient / $10^{-9} \text{ cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	Product ions (%)	Proposed neutral products	$\Delta_r H^\circ_{298} / \text{kJ mol}^{-1}$
H <sub>3</sub> O <sup>+</sup> (6.27)	[2.6]	No reaction		
SF <sub>3</sub> <sup>+</sup> (8.26)	[1.6]	No reaction		
CF <sub>3</sub> <sup>+</sup> (9.03)	1.5 [1.7]	CH <sub>2</sub> Cl <sup>+</sup> (84) CHClF <sup>+</sup> (10) CH <sub>2</sub> F <sup>+</sup> (6)	CF <sub>4</sub> CHF <sub>3</sub> CClF <sub>3</sub>	-118 <sup>a</sup> -98 <sup>a</sup> -19 <sup>a</sup>
CF <sup>+</sup> (9.10)	1.7 [2.2]	CH <sub>2</sub> Cl <sup>+</sup> (96) CH <sub>2</sub> F <sup>+</sup> (4) CHClF <sup>+</sup> (trace)	CF <sub>2</sub> CClF CHF	-95 -8 <sup>b</sup> +14 <sup>c</sup>
NO <sup>+</sup> (9.26)	[2.2]	No reaction		
SF <sub>5</sub> <sup>+</sup> (9.55)	0.7 [1.5]	CH <sub>2</sub> Cl <sup>+</sup> (100)	SF <sub>6</sub>	-29 <sup>d</sup>
NO <sub>2</sub> <sup>+</sup> (9.59)	[1.9]	No reaction		
SF <sub>2</sub> <sup>+</sup> (10.17)	[1.7]	No reaction		
SF <sup>+</sup> (10.25)	1.5 [1.9]	CH <sub>2</sub> F <sup>+</sup> (45) CHClF <sup>+</sup> (42) CH <sub>2</sub> Cl <sup>+</sup> (13)	SClF SHF SF <sub>2</sub>	+97 + $\Delta_r H^\circ_{298}$ (SClF) <sup>e</sup> +7 + $\Delta_r H^\circ_{298}$ (SHF) <sup>e</sup> -73 <sup>e,f</sup>
CF <sub>2</sub> <sup>+</sup> (11.43)	1.6 [1.9]	CH <sub>2</sub> Cl <sup>+</sup> (85) CH <sub>2</sub> F <sup>+</sup> (15) CHClF <sup>+</sup> (trace)	CF <sub>3</sub> CClF <sub>2</sub> CHF <sub>2</sub>	-167 <sup>g,h</sup> -106 <sup>g,i</sup> -154 <sup>g</sup>
SF <sub>4</sub> <sup>+</sup> (11.92)	1.1 [1.6]	CH <sub>2</sub> Cl <sup>+</sup> (100)	SF <sub>5</sub>	-83 <sup>j,k</sup>
O <sub>2</sub> <sup>+</sup> (12.07)	2.1 [2.2]	CH <sub>2</sub> ClF <sup>+</sup> (61) CHClF <sup>+</sup> (31) CH <sub>2</sub> Cl <sup>+</sup> (8)	O <sub>2</sub> HOO FOO	-34 -158 +82, +60, +37 <sup>l</sup>
Xe <sup>+</sup> (12.13/13.44) <sup>m</sup>	1.3 [1.5]	CH <sub>2</sub> ClF <sup>+</sup> (57) CHClF <sup>+</sup> (29) CH <sub>2</sub> F <sup>+</sup> (13) CH <sub>2</sub> Cl <sup>+</sup> (1)	Xe Xe + H Xe + Cl Xe + F	-40, -166 <sup>m</sup> +52, -74 <sup>m</sup> +46, -81 <sup>m</sup> +130, +4 <sup>m</sup>
N <sub>2</sub> O <sup>+</sup> (12.89)	1.5 [2.0]	CH <sub>2</sub> ClF <sup>+</sup> (54)  CH <sub>2</sub> F <sup>+</sup> (39)  CH <sub>2</sub> Cl <sup>+</sup> (7)	N <sub>2</sub> + O or N <sub>2</sub> O  N <sub>2</sub> + OCl or N <sub>2</sub> O + Cl  N <sub>2</sub> + OF or	+54 or -113  -130 or -28  +4 or

			N <sub>2</sub> O + F	+56
O <sup>+</sup> (13.62)	2.2 [2.8]	CH <sub>2</sub> F <sup>+</sup> (63) CH <sub>2</sub> Cl <sup>+</sup> (25) CHClF <sup>+</sup> (8) CH <sub>2</sub> ClF <sup>+</sup> (4)	OCl OF O OH	-367 -233 -183 -519
CO <sub>2</sub> <sup>+</sup> (13.78)	1.7 [2.0]	CH <sub>2</sub> F <sup>+</sup> (73) CH <sub>2</sub> Cl <sup>+</sup> (12) CHClF <sup>+</sup> (8) CH <sub>2</sub> ClF <sup>+</sup> (7)	CO <sub>2</sub> + Cl CO <sub>2</sub> + F CO <sub>2</sub> + H CO <sub>2</sub>	-112 -28 -106 -198
Kr <sup>+</sup> (14.00)	1.4 [1.7]	CH <sub>2</sub> F <sup>+</sup> (83) CH <sub>2</sub> Cl <sup>+</sup> (11) CHClF <sup>+</sup> (3) CH <sub>2</sub> ClF <sup>+</sup> (3)	Kr + Cl Kr + F Kr + H Kr	-135 -51 -128 -220
CO <sup>+</sup> (14.01)	2.3 [2.3]	CH <sub>2</sub> F <sup>+</sup> (93) CH <sub>2</sub> Cl <sup>+</sup> (4) CHClF <sup>+</sup> (2) CH <sub>2</sub> ClF <sup>+</sup> (1)	COCl COF COH CO	-209 -192 -193 -221
N <sup>+</sup> (14.53)	3.3 [3.0]	CH <sub>2</sub> F <sup>+</sup> (55) CH <sub>2</sub> Cl <sup>+</sup> (19) CHClF <sup>+</sup> (16) CH <sub>2</sub> ClF <sup>+</sup> (10)	NCl NF NH N	-466 <sup>n</sup> -405 -494 -271
N <sub>2</sub> <sup>+</sup> (15.58)	2.1 [2.3]	CH <sub>2</sub> F <sup>+</sup> (73) CH <sub>2</sub> Cl <sup>+</sup> (20) CHClF <sup>+</sup> (4) CH <sub>2</sub> ClF <sup>+</sup> (3)	N <sub>2</sub> + Cl N <sub>2</sub> + F N <sub>2</sub> + H N <sub>2</sub>	-287 -203 -280 -372
Ar <sup>+</sup> (15.76)	2.6 [2.0]	CH <sub>2</sub> F <sup>+</sup> (79) CH <sub>2</sub> Cl <sup>+</sup> (17) CHClF <sup>+</sup> (4)	Ar + Cl Ar + F Ar + H	-305 -221 -298
F <sup>+</sup> (17.42)	2.5 [2.6]	CH <sub>2</sub> Cl <sup>+</sup> (81) CH <sub>2</sub> F <sup>+</sup> (17) CH <sub>2</sub> ClF <sup>+</sup> (2)	F <sub>2</sub> ClF F	-539 -715 -550
Ne <sup>+</sup> (21.56)	2.0 [2.6]	CHF <sup>+</sup> (36) Cl <sup>+</sup> (21) CH <sub>2</sub> <sup>+</sup> (14) CF <sup>+</sup> (8)  CH <sub>2</sub> F <sup>+</sup> (7) CCl <sup>+</sup> (6) CHCl <sup>+</sup> (4) CHClF <sup>+</sup> (3) CH <sub>2</sub> Cl <sup>+</sup> (1) CH <sub>2</sub> ClF <sup>+</sup> (trace)	Ne + HCl Ne + CH <sub>2</sub> F Ne + ClF Ne + H <sub>2</sub> + Cl or Ne + HCl + H Ne + Cl Ne + HF + H Ne + HF Ne + H Ne + F Ne	-789 -480 -482 -563 or -558 -864 -630 -844 -857 -780 -949

<sup>a</sup>  $\Delta_f H^\circ_{298}(\text{CF}_3^+) = +406 \text{ kJ mol}^{-1}$ .<sup>35</sup> <sup>b</sup>  $\Delta_f H^\circ_{298}(\text{CClF}) = +31 \text{ kJ mol}^{-1}$ .<sup>36</sup> <sup>c</sup>  $\Delta_f H^\circ_{298}(\text{CHF}) = +143 \text{ kJ mol}^{-1}$ .<sup>36</sup> <sup>d</sup>  $\Delta_f H^\circ_{298}(\text{SF}_5^+) = +29 \text{ kJ mol}^{-1}$ .<sup>37</sup> <sup>e</sup>  $\Delta_f H^\circ_{298}(\text{SF}^+) = +998 \text{ kJ mol}^{-1}$ .<sup>23</sup> <sup>f</sup>  $\Delta_f H^\circ_{298}(\text{SF}_2) = -295 \text{ kJ mol}^{-1}$ .<sup>23</sup> <sup>g</sup>  $\Delta_f H^\circ_{298}(\text{CF}_2^+) = +922 \text{ kJ mol}^{-1}$ , calculated from  $\Delta_f H^\circ_{298}(\text{CF}_2) + \text{IE}(\text{CF}_2)$ .<sup>21</sup> <sup>h</sup>  $\Delta_f H^\circ_{298}(\text{CF}_3) = -466 \text{ kJ mol}^{-1}$ .<sup>35</sup> <sup>i</sup>  $\Delta_f H^\circ_{298}(\text{CClF}_2) = -279 \text{ kJ mol}^{-1}$ .<sup>38</sup> <sup>j</sup>  $\Delta_f H^\circ_{298}(\text{SF}_4^+) = +389 \text{ kJ mol}^{-1}$ .<sup>23</sup> <sup>k</sup>  $\Delta_f H^\circ_{298}(\text{SF}_5) = -915 \text{ kJ mol}^{-1}$ .<sup>40</sup> <sup>l</sup> The three values quoted are for the enthalpy of reaction at 298 K involving the  $\nu = 0, 1,$  and  $2$  levels of the ground electronic state of  $\text{O}_2^+$ , using  $\text{O}_2^+$  ground state vibrational spectroscopic constants.<sup>21</sup> <sup>m</sup> The two values quoted are for the enthalpy of reaction at 298 K involving the  $^2\text{P}_{3/2}$  and  $^2\text{P}_{1/2}$  spin-orbit states of  $\text{Xe}^+$ .<sup>12</sup> <sup>n</sup>  $\Delta_f H^\circ_{298}(\text{NCl}) = +314 \text{ kJ mol}^{-1}$ .<sup>39</sup>

## ***Figure Captions***

***Figure 1*** Comparison of the ionic products from ion-molecule studies of  $\text{CHCl}_2\text{F}$  with TPEPICO photoionization branching ratios over the energy range 12 – 24 eV. The SIFT branching ratios are corrected so that the sum of the relevant data equals unity.

***Figure 2*** Comparison of the ionic products from ion-molecule studies of  $\text{CHClF}_2$  with TPEPICO photoionization branching ratios over the energy range 12 – 22 eV. The SIFT branching ratios are corrected so that the sum of the relevant data equals unity.

***Figure 3*** Comparison of the ionic products from ion-molecule studies of  $\text{CH}_2\text{ClF}$  with TPEPICO photoionization branching ratios over the energy range 12 – 24 eV. The SIFT branching ratios are corrected so that the sum of the relevant data equals unity.

Figure 1

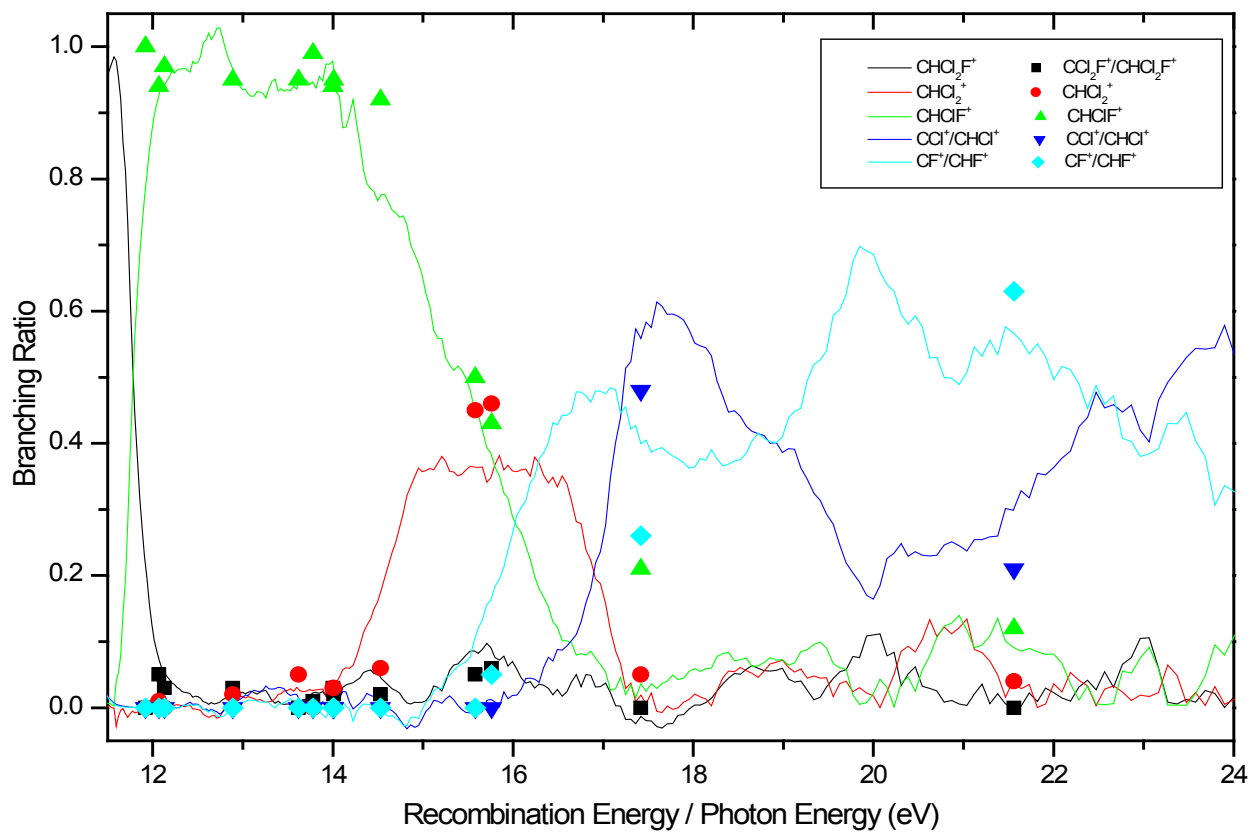


Figure 2

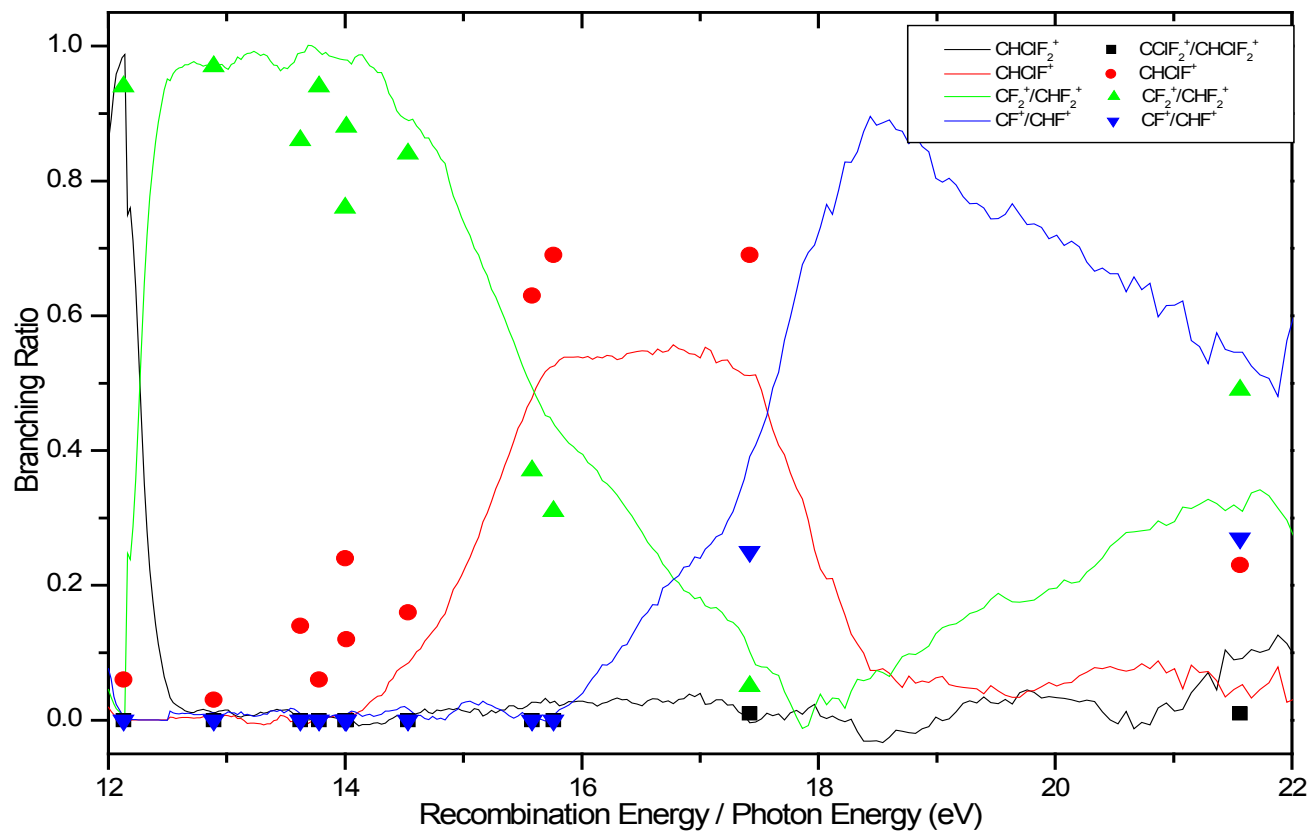




Figure 3

