

PHOTOELECTRON PHOTOION COINCIDENCE  
STUDY OF THE FRAGMENTATION OF VALENCE  
STATES OF CHF<sub>2</sub> – CH<sub>3</sub><sup>+</sup> IN THE RANGE 12–25 eV

Zhou, Weidong; Tuckett, Richard P.; Chim, Raymond; Collins, DJ

DOI:

[10.1142/S0217979209052868](https://doi.org/10.1142/S0217979209052868)

*Citation for published version (Harvard):*

Zhou, W, Tuckett, RP, Chim, R & Collins, DJ 2009, 'PHOTOELECTRON PHOTOION COINCIDENCE STUDY OF THE FRAGMENTATION OF VALENCE STATES OF CHF<sub>2</sub> – CH<sub>3</sub><sup>+</sup> IN THE RANGE 12–25 eV', *International Journal of Modern Physics B*, vol. 23, no. 14, pp. 3073-3087. <https://doi.org/10.1142/S0217979209052868>

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Weidong Zhou, Ray Y L Chim, Dan J Collins and Richard P. Tuckett

*Int. J of Mod. Phys. B. (World Scientific)*, (2009) **23(14)**, 3073-3087

DOI : 10.1142/S0217979209052868

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Professor Richard Tuckett (University of Birmingham) / July 2011

## Photoelectron photoion coincidence study of the fragmentation of valence states of $\text{CHF}_2\text{-CH}_3^+$ in the range 12-25 eV

Weidong Zhou<sup>1,2</sup>, Ray Y. L. Chim<sup>2</sup>, D. J. Collins<sup>2</sup>, Richard P. Tuckett<sup>2</sup>

<sup>1</sup> Zhejiang Normal University, Jinhua, Zhejiang, 321004, China

<sup>2</sup> School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

Number of pages : 14 (excluding tables and figure captions)

Number of tables : 2

Number of figures : 4

Author for correspondence: Dr Weidong Zhou

[email: [wdzhou@zjnu.cn](mailto:wdzhou@zjnu.cn), Fax: +86 579 229 8188]

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### **Abstract**

Using vacuum ultraviolet radiation from a synchrotron source, threshold photoelectron photoion coincidence (TPEPICO) spectroscopy has been used to study the dissociative photoionisation of  $\text{CHF}_2\text{-CH}_3$ , in the photon energy from 11.8 eV to 24.8 eV. Combining with *ab initio* molecular orbital calculation, fragmentation process and fragmental mechanism of the valence states of parent ion are discussed. For single bond cleavage process, a statistical mechanism might govern the C-C bond cleavage, while the kinetic energy release derived from channel  $\text{CHF}_2\text{-CH}_3^+ \rightarrow \text{CH}_3\text{-CHF}^+ + \text{F} + \text{e}^-$  shows evidence for impulsive mechanism. A two-step increase of signal  $\text{CF}_2\text{-CH}_3^+ / \text{CHF}_2\text{-CH}_2^+$  was observed. The two-step is due to the formation of ion  $\text{CF}_2\text{-CH}_3^+ / \text{CHF}_2\text{-CH}_2^+$  through two different dissociation channels. Both computed molecular orbital character and related G2 dissociation energy support the assumption.

The ionisation threshold of  $12.02 \pm 0.04$  eV measured from the TPES and the appearance energies (AEs) identified from the ion yield curves are presented. New or refined upper limit values of enthalpy of formation at 298K for ion  $\text{CHF}_2^+$ ,  $\text{CF}_2\text{-CH}_3^+$  and  $\text{CHF-CH}_3^+$  are derived.

**Key words:** TPEPICO, fragmentation,  $\text{CHF}_2\text{-CH}_3^+$

## 1. Introduction

Among the HFCs group  $C_2H_nF_{6-n}$ , 1, 1 difluoroethane is one of the potential alternative compounds to chlorofluorocarbons which deplete ozone [1]. In last decade,  $CHF_2-CH_3$  has attracted a lot of attention both in science and industry [2-6]. Because of its possible application as refrigerant and its possible effect on global warming, most of the previous researches have concentrated on its thermodynamic property, structure, infrared spectrum and reactions in atmosphere. Only a few early papers have been published which concern the dissociative ionisation and decay mechanism of valence states of  $CHF_2-CH_3$  using VUV photoionisation method [7-12]. In the six reported works, three of them are concerned with the fragmentation by electron impact ionisation (EI). In electron impact ionisation studies, the appearance energies of many ions and thus their thermodynamic parameters were determined [8, 11, 12]. However, due to the relatively poor energy resolution of electron beams used in these works, the accuracy of the derived thermodynamics properties is rather limited. Also, the appearance energies determined by electron impact ionisation are normally large than those determined by photoionisation. The only photoionisation (PI) study on the fragmentation of  $CHF_2-CH_3$  with photoionisation mass spectrometry (PIMS) and threshold photoelectron spectroscopy (TPES) used the hydrogen many-line pseudo-continuum and the helium Hopfield continuum as ionisation radiation sources [7]. The interests of Heinis *et al* [7] were mainly to determine appearance energies and heats of formation of the fragment cations, although they also observed some isolated-state behaviour of electronic states of the parent cation at photon energies above 16 eV.

As part of a series in our investigations on the fragmentation mechanism of valence electronic state of hydrofluoroethanes (HFCs) using threshold photoelectron photoion coincidence (TPEPICO) spectroscopy and synchrotron radiation as a tunable VUV photoionisation source, several separated investigations have carried out on five HFCs; pentafluoroethane [13], the two isomers of tetrafluoroethane [14], and the two isomers of trifluoroethane [15]. In this paper a comprehensive study on the mechanism of valence state fragmentation of  $CHF_2-CH_3^+$  by TPEPICO spectroscopy is presented. The threshold photoelectron spectrum (TPES) and state-selected fragmentation studies of the parent ions are presented. Breakdown diagrams, yielding the formation probability of fragmental ions as a function of photon energy, are

obtained. The mean translational kinetic energy releases for unimolecular fragmentation proceeding *via* a single-bond cleavage are determined, and compared with the predictions of statistical and dynamical impulsive models. Also, some thermochemical data of the observed fragmental cations have been derived or refined.

## 2. Experimental method

The TPEPICO apparatus has been described in detail elsewhere [13, 16, 17]. Hence it is only briefly outlined here. Synchrotron radiation from a 2 GeV electron storage ring at the Daresbury Laboratory is monochromatized by using a 1 m Seya-Namioka monochromator equipped with two gratings, covering the energy range 8-40 eV. The majority of the experiments for CHF<sub>2</sub>-CH<sub>3</sub> were performed using the lower-energy grating (range 150-60 nm (8-21 eV), blaze at 90 nm) with an optical resolution of 0.3 nm. For photon energy higher than 20 eV, the higher-energy grating (range 105-30 nm (12-40 eV), blaze at 55 nm) was used with the same resolution. With the higher-energy grating, the effects of second-order radiation are insignificant for  $\lambda < 95$  nm, for the lower-energy grating for  $\lambda < 120$  nm. The optical resolution employed for the experiment is 0.3 nm. The wavelength of the monochromator was carefully calibrated with the known ionisation potential of Ar at 15.759 and 15.937 eV, respectively. The monochromatized VUV radiation is admitted into an interaction region through a capillary. The photon flux is monitored, using a photomultiplier tube (PMT) attached via a sodium-salicylate-coated window behind the interaction region.

Threshold photoelectrons and positive ions produced by the VUV photoionization / fragmentation were extracted in opposite directions through a 20 Vcm<sup>-1</sup> electric field applied across the interaction region, and detected separately by a channeltron electron multiplier and microchannel plates. The threshold electron analyser with an energy resolution of 10 meV was used to detect threshold electrons [17]. It consists of a cylindrical electrostatic lens designed with large chromatic aberrations and a 127° post-analyser to reject energetic electrons emitted on axis. Positive ions extracted from the interaction region are detected through a linear time-of-flight (TOF) mass spectrometer, which consists of a two-stage acceleration region configured to satisfy the space focusing condition, followed by a field-free region of length 186 mm. Pulses from the electron and ion detectors pass through a discriminator and pulse shaping circuits to a time-to-digital converter (TDC) configured in the

multi-hit mode. The electrons signal provide the start and the ions signal provide the stop pulses, allowing signals from the same ionisation process to be detected in coincidence way.

TPEPICO spectra can be recorded either continuously as a function of photon energy or at a fixed energy. In the scanning-energy mode, flux-normalized TPEPICO spectra are recorded as a three dimensional histogram, where the coincidence count is plotted against both the ion flight time and photon energy. By taking the cross section from the histogram in different ways, we can obtain two kinds of diagram. A cut through the map at fixed photon energy gives the time of flight mass spectrum (TOF-MS), which enables us to identify the fragmental ions formed in the dissociative photoionisation process. A background-subtracted cut taken through the histogram at a fixed ion flight time corresponding to a mass peak at TOF-MS gives an ion yield curve, and several similar cuts are taken according to the produced ions. Breakdown diagram can be calculated through normalisation of the ion intensities at every wavelength. This gives the formation probability of the product ions as a function of the photon energy. In the scanning-energy mode, the threshold electron and total ion counts produced during photoionisation are also recorded, providing a TPES and total ion yield curve respectively. Fixed-energy TOF spectra are measured, generally at energies corresponding to peaks seen in the TPES, using a TOF resolution as high as the signal level permits. Fragment ions often have enough translational energy released for the peaks to be substantially broadened. It is then possible to obtain kinetic energy release distributions (KERDs) and hence total mean kinetic energy releases  $\langle KE \rangle_T$  from analysis of the TOF shapes [18, 19].

The sample gas CHF<sub>2</sub>-CH<sub>3</sub> was obtained commercially (Fluorochem Ltd., UK), with a stated purity of >99% and used without further purification. The sample was injected through a needle valve. The typical operating pressure is about  $5 \times 10^{-5}$  mbar, several orders of magnitude above the base pressure of  $5 \times 10^{-8}$  mbar in the chamber.

### 3. Computational Details and Results

#### 3.1 Computational method

*Ab initio* molecular orbital calculations have been carried out for CHF<sub>2</sub>-CH<sub>3</sub> in the neutral ground state and ground cationic state, using the quantum chemistry program of Gaussian 98. The molecular structures for all species were optimized using the second-order Møller-Plesset theory (MP2) with the 6-31G(d) basis set, and all electrons were included at the MP2(full)/6-

31G(d) level. The MP2(full)/6-31G(d) structures were then employed for energy calculations according to the Gaussian-2 ( G2 ) theoretical procedure [20] .

The G2 theoretical procedure involves single-point total energy calculations at the MP4/6-311G(d,p), QCISD(T)/6-311g(d,p), MP4/6-311G(d,p), MP4/6-311G(2df,p), and MP2/6-311G(3df,2p) levels. A small empirical correction is employed to include the high-level correlation effects in the calculations of the total electronic energies ( $E_e$ ). The HF/6-31G(d) harmonic vibration frequencies, scaled by 0.8929, are applied for zero-point vibration energy (ZPVE) corrections to obtain the total energies at 0 K ( $E_0 = E_e + \text{ZPVE}$ ). The total enthalpies at 298 K ( $H_{298}$ ) for molecular species are calculated using the scaled HF/6-31G(d) harmonic frequencies. The agreement between G2 and experimental result is usually well within  $\pm 0.15$  eV (or about 15 KJ / mol) [20].

### 3.2 Theoretical results

The structure optimisation of  $\text{CHF}_2\text{-CH}_3$  and  $\text{CHF}_2\text{-CH}_3^+$  has been calculated at the MP2/6-31(d) level. Both of them have a staggered structure of  $C_s$  symmetry with four atoms (H, C, C, H) lying on the symmetry plan. The optimised geometries of  $\text{CHF}_2\text{-CH}_3$  are very close to the reported electron diffraction results [21]. At this level of theory, the main geometries changes after ionisation are the increase of 0.37 Å in the C—C bond length, the decrease of 0.08 Å in the C-F bond length, in addition, both the non-planar  $\text{CHF}_2$  and  $\text{CH}_3$  group become approximately planar.

The electronic configuration of  $\text{CHF}_2\text{-CH}_3$  ( $X^1A'$ ) is  $\dots 5(A'')^2 9(A')^2 6(A'')^2 10(A')^2 11(A')^2$ , where the numbering includes core orbitals. The structure of the neutral molecule and its three highest outer- valence molecular orbitals (MOs) are shown in figure 1. It is difficult to give a simple characterisation of these MOs due to their hybridised nature. The  $11(A')$  highest occupied molecular orbital (HOMO) is mainly a  $\pi^*$  anti-bonding orbital centred at the fluorinated carbon with a node in the CFF plane. It has strong C-C  $\sigma$ -bonding character and some C-H  $\sigma$ -bonding character on the symmetry plan. Loss of an electron from this orbital, yields the ground cationic state, will lead to a significant increase of C-C bond length and a small decrease in the C-F bond length. The orbital  $10(A')$ , which next to the highest occupied molecular orbital (*i.e.*, HOMO-1) is largely localized on the  $\text{CH}_3$  group with some  $\pi$  bonding character. It is bonding both in the C-H bond on the symmetry plan and the H-H bond between other two H atoms on the  $\text{CH}_3$  group. The (HOMO-2) orbital  $6(A'')$  is also

of a  $\pi$  bonding orbital but localized on the  $\text{CHF}_2$  group and with a node on symmetry plane. The character of both  $10(A')$  and  $6(A'')$  orbitals indicate that loss of a hydrogen atom might be a favoured dissociation process, although this process is only a minimum or neglected dissociation channel in other highly fluorinated ethanes [13,14,15].

G2 energy calculations are carried out on the ground state for  $\text{CHF}_2\text{-CH}_3$  and then for  $\text{CHF}_2\text{-CH}_3^+$  respectively. From the energetic difference at the ground states, the adiabatic ionisation energy of 11.82 eV is obtained. Similarly, vertical ionisation energy (VIE) was calculated on the ground state, but this time the G2 energy for  $\text{CHF}_2\text{-CH}_3^+$  was calculated at the same ground state geometries of  $\text{CHF}_2\text{-CH}_3$ , and a VIE value 12.83 eV is deduced.

## 4. Discussion

### 4.1 TPES

The TPES of  $\text{CHF}_2\text{-CH}_3$  was recorded from 50 – 105 nm (12 ~ 25 eV) at a resolution of 0.3 nm (Figure 2), both the medium and high energy gratings were employed, and the spectra merged. Following normal spectroscopic convention, the state at lowest energy, corresponding to electron removal from the HOMO, is labelled the  $\tilde{X}$  state; the next lowest energy state, corresponding to electron removal from the (HOMO-1), the  $\tilde{A}$  state; the next the  $\tilde{B}$  state *etc.* The vertical ionisation energies (VIEs) for the  $\tilde{X}$ ,  $\tilde{E}$ ,  $\tilde{F}$  and  $\tilde{G}$  states are determined to be  $12.89 \pm 0.05$ ,  $17.71 \pm 0.07$ ,  $18.79 \pm 0.08$  and  $21.9 \pm 0.1$  eV, respectively. The unresolved  $\tilde{A}$ ,  $\tilde{B}$ ,  $\tilde{C}$  and  $\tilde{D}$  states of parent ion can tentatively be assigned VIEs of  $14.12 \pm 0.05$ ,  $14.67 \pm 0.05$ ,  $15.12 \pm 0.06$  and  $18.79 \pm 0.08$  eV, respectively. The ground ionic state is broad and separated from higher-lying electronic states; this is consistent with the large geometrical changes that will occur after the removal of an electron from the HOMO,  $11(A')$  which is assumed to be mainly C-C  $\sigma$ -bonding in character.

The TPES shows that the onset of signal occurs at  $12.02 \pm 0.04$  eV. This value is 0.20 eV higher than the calculated AIE of  $\text{CHF}_2\text{-CH}_3$ , and 0.16 eV higher than that reported by Heinis *et al.*[7] The former discrepancy shows the limitation of using the TPES to determine the ionization threshold of a molecule that has a large geometry change after ionization, and hence a small Franck-Condon factor at threshold. [22, 23] Lifshitz *et al.* [8] have also researched the ionisation process by means of EI ionisation, and they reported an ionisation threshold of 12.68 eV. Due to the known uncertainty of such electron impact studies, the



results obtained here and by Heinis *et al.* [7] should be more reliable. The observed VIE in our TPES is  $12.89 \pm 0.04$  eV, agrees well with the value 12.8 eV reported by Sauvageau *et al.* in their HeI PES spectrum [10], and is consistent with our computed G2 VIE value of 12.83 eV.

When comparing the TPES recorded here with that of the He I PES obtained by Sauvageau *et al.* [10], the two spectra agree reasonable well. It can be useful to compare the relative intensities of the peaks in the threshold photoelectron and He I photoelectron spectra. As He I spectra are recorded with a fixed-energy photon source, this is likely to lead to electrons arising only from direct ionisation to be detected. The threshold photoelectron spectrum is measured by scanning the energy of a continuum radiation source. This can lead to electrons arising from autoionisation processes being detected, provided that their energy is close to threshold. It is noted that the main difference between the two spectra is the relative intensity of the second band from 14-16 eV, which corresponds to the unresolved  $\tilde{A}$ ,  $\tilde{B}$ ,  $\tilde{C}$  and  $\tilde{D}$  states of the parent ion. The intensity is significantly lower under threshold conditions. This could be due to either a change in the relative ionisation cross section between excitation at threshold and non-resonant He I (21.22 eV) radiation, or as mentioned above to autoionisation effects. The former is suggested as the explanation. As described elsewhere, [13, 24] a comparison of the total ion yield of CHF<sub>2</sub>-CH<sub>3</sub> with the integrated TPES will reveal peaks in the TPES which occur *via* an autoionisation mechanism. The good agreement of our integrated TPES and total ion yield over this energy range, and the absence of such extra peaks, indicates that autoionisation is not an important process in this energy range.

#### 4.2 Fragmentation of valence states of CHF<sub>2</sub>-CH<sub>3</sub><sup>+</sup>

A TPEPICO spectrum in the scanning-energy mode was recorded for CHF<sub>2</sub>-CH<sub>3</sub> from 12-25 eV at an optical resolution of 0.3 nm and an ion TOF resolution of 32 ns. The fragments CF<sub>2</sub>-CH<sub>3</sub><sup>+</sup>, CHF-CH<sub>3</sub><sup>+</sup>, CHF<sub>2</sub><sup>+</sup> and CH-CH<sub>2</sub><sup>+</sup> were detected, and their yields are shown in Figure 3. From these curves, a breakdown diagram has been constructed (Figure 4), showing the relative ion abundance as a function of photon energy from dissociative photoionisation of CHF<sub>2</sub>-CH<sub>3</sub>.

From the ion yield curves and the breakdown diagram, it can be seen that CF<sub>2</sub>-CH<sub>3</sub><sup>+</sup> appears weakly at the lowest energy, then with increasing energy the two fragment ions CHF<sub>2</sub><sup>+</sup> and CHF-CH<sub>3</sub><sup>+</sup> are observed. These three ions are the main fragments within the energy range 12-16 eV. At higher energy, ion CH-CH<sub>2</sub><sup>+</sup> appears and becomes the main fragment in the range 18-20 eV. We comment that that by using a TOF resolution of only 32 ns, a definitive

determination of the number of hydrogen atoms in a fragment ion can be problematic, However, by careful analysis of the absolute TOF values, there is confidence that the above four assignments are correct.

All the four fragments have been observed previously either in electron impact studies [8, 25] or photoionisation mass spectrum studies [7]. Either the weak coincident ion signal or the fact that the mass of the parent ion and  $\text{CF}_2\text{-CH}_3^+$  are so close leads to the absence of parent ion signal in our coincidence spectrum. We note, however, that Heinis *et al.*[7] and Lifshitz *et al.*[8] have observed parent ion very weakly in their experiments.

The appearance energy (AE) at 298 K of each fragment ion has been determined from the extrapolation of the linear portion of the ion yield to zero signal level. At the resolution of our experiment, this is equivalent to the first onset of signal. No corrections have been made for possible reverse potential barriers or kinetic shifts in determining the AEs. The AE values estimated in this way only serve as upper limits. The ions and their AEs identified from our experiment are listed in table 1, along with the values measured from other researches. The error bars are also listed. These errors reflect either the bandwidth of our monochromator or the wavelength interval of the data points for performing the measurement. We have used the procedure of Traeger and McLoughlin to convert the observed AEs into an enthalpy of the unimolecular reaction at 298 K,  $\Delta_r H^0_{298}$ . Full details are given elsewhere[13, 26]. The  $\Delta_r H^0_{298}$  for dissociative photoionization reaction calculated by G2 procedure are also listed in the table 1. From these AE values, the upper limit of enthalpies of formation of different ions produced from fragmentation of  $\text{CHF}_2\text{-CH}_3^+$  can be estimated. And the derived enthalpies of formation of the ions are listed in table 1 either, together with the literature values. The enthalpies of formation ( $\Delta_f H^0_{298}$ ) we used for all of the above calculation are taken from Chase [27] or Lias *et al.*, [28] the exception being the value for  $\text{CHF}_2\text{-CH}_3$  [29].

It appears through a rough comparison that the data of Heinis *et al.* and Williamson *et al.*, which were measured by photoionization method, are in good agreement with our results, whereas the data of Lifshitz and co-worker measured by electron impact ionisation method are higher. This is understandable since it is known that the EI ionisation method often overestimates AEs of both parent and fragmental ions. Heinis and co-worker have also reported an AE value of 11.87 eV for  $\text{CHF-CH}_3^+$  and 15.07 eV for  $\text{CH-CH}_2^+$  arise from the ion pair formation. As in TPEPICO spectrum, the ions are measured in coincidence with

threshold electrons. Ion pair formation cannot be detected through our equipment and the two onsets cannot be observed in our ion yield curves.

From Figure 3, the first cation observed from the ground state of the parent ion is  $\text{CF}_2\text{-CH}_3^+$ , with an appearance potential of  $12.02 \pm 0.04$  eV. The signal is relatively weak. Using the method of Traeger and McLoughlin, this  $\text{AE}_{298}$  can be converted into an upper limit for  $\Delta_r H^\circ_{298}$  for the reaction  $\text{CHF}_2\text{-CH}_3 \rightarrow \text{CF}_2\text{-CH}_3^+ + \text{H} + \text{e}^-$  of 12.19 eV. Using values for the 298K enthalpy of formation of  $\text{CHF}_2\text{-CH}_3$  and H [26, 28], we determine  $\Delta_r H^\circ_{298}(\text{CF}_2\text{-CH}_3^+)$  to be  $452 \pm 4$  kJ mol<sup>-1</sup>, if it is assumed that this fragment ion turns on at its thermochemical threshold. This value agrees well with the G2 value of 443 kJ mol<sup>-1</sup>. The indication is that H-loss from  $\text{CHF}_2\text{-CH}_3^+$  occurs from the  $\text{CHF}_2$ - group, and the H-loss does turn on at the thermochemical threshold.

Over the Franck-Condon region of the ground state of the parent ion, the  $\text{CF}_2\text{-CH}_3^+$  signal roughly matches that of the TPES up to the maximum of the ground state. The  $\text{CF}_2\text{-CH}_3^+$  signal decreases until 13.40 eV, then another slow increase can be seen. The emergence of this ‘second-step’ corresponds with the onset of the first excited state of  $\text{CHF}_2\text{-CH}_3^+$ . Heinis et al. [7] noted an interval of 1.67 eV between the onset and this ‘second-step’. They concluded that this ‘second-step’ was due either to the formation of  $\text{CHF}_2\text{-CH}_2^+$  or to  $\text{CF}_2\text{-CH}_3^+$  via a new channel involving a 1, 2 hydrogen migration. The energy difference between the two steps in this work is 1.29 eV, slightly lower than that obtained in reference [7]. It is felt that the second step is possibly due to a new dissociation channel to  $\text{CHF}_2\text{-CH}_2^+$ . There are two reasons to support the point. Firstly, G2 calculation indicates that the difference of reaction energy for  $\text{CHF}_2\text{-CH}_3 \rightarrow \text{CF}_2\text{-CH}_3^+ + \text{H} + \text{e}^-$  (12.18 eV) and  $\text{CHF}_2\text{-CH}_3 \rightarrow \text{CHF}_2\text{-CH}_2^+ + \text{H} + \text{e}^-$  (13.51 eV), is 1.33 eV, which is consistent with the energy difference between the “two steps” observed here. Secondly, molecular orbital calculation shows that the first excited state( $\tilde{\text{A}}$ ) of  $\text{CHF}_2\text{-CH}_3^+$  comes from lose of an electron from an orbital largely consists of C-H bond localized on the  $\text{CH}_3$  group. The second step of  $\text{CF}_2\text{-CH}_3^+ / \text{CHF}_2\text{-CH}_2^+$  signal exactly corresponding to the onset of  $\tilde{\text{A}}$  states. It is then reasonable to assume parent ion loss of a hydrogen atom from group  $\text{CH}_3$  to form  $\text{CHF}_2\text{-CH}_2^+$ . To form another isomer  $\text{CHF-CH}_2\text{F}^+$ , although energetically allowed, seems unlikely according to the MO character.

The  $\text{CHF}_2^+$  fragment has an  $\text{AE}_{298}$  of  $12.73 \pm 0.04$  eV. This fragment is the most intense and is the dominant fragment from 13.7 eV to 16.0 eV. Applying the Traeger et al. correction to this  $\text{AE}_{298}$  value, we determine  $\Delta_r H^\circ_{298}$  for the reaction  $\text{CHF}_2\text{CH}_3 \rightarrow \text{CHF}_2^+ + \text{CH}_3 + \text{e}^-$  to be

$12.89 \pm 0.04$  eV. This is in agreement with the value obtained, 12.96 eV, from established  $\Delta_f H^\circ_{298}$  values for reactants and products [27, 28, 29]. The one exception is the value used for  $\text{CHF}_2^+$  where we use a more recent value,  $604 \text{ kJ mol}^{-1}$ , from our own work [13]. This value for  $\Delta_f H^\circ_{298}$  is also in good agreement with the value 12.86 eV from G2 calculation. All this information suggests that the C-C bond breaks at the thermochemical threshold for reaction to form  $\text{CHF}_2^+ + \text{CH}_3 + e^-$ . The two ions,  $\text{CF}_2\text{-CH}_3^+$  and  $\text{CHF}_2^+$  appear within the ground ionic state, are consistent with that the HOMO is largely of C-C bonding and some C-H bonding character localized on  $\text{CHF}_2$  group.

The  $\text{CHF-CH}_3^+$  fragment has an  $\text{AE}_{298}$  of  $13.50 \pm 0.05$  eV, corresponding to an upper limit of  $\Delta_f H^\circ_{298}$  for the reaction  $\text{CHF}_2\text{-CH}_3 \rightarrow \text{CHF-CH}_3^+ + \text{F} + e^-$  of 13.62 eV. This onset is relatively shallow and weak, but there is a second more rapid onset at  $14.23 \pm 0.05$  eV. *Ab initio* calculations indicate that it needs almost equal energy to form two isomers of  $\text{CHF-CH}_3^+$  and  $\text{CH}_2\text{F-CH}_2^+$ . The energy ca. 0.73 eV difference cannot arise from isomerization. It is presumed that this second increase in  $\text{CHF-CH}_3^+$  signal is possibly due to the fact that the molecular orbital from which the electron is removed has some F lone-pair characteristic; state-selected dissociation would then favour production of  $\text{CHF-CH}_3^+$ . Using the first onset at 13.50 eV, having applied the Traeger *et al.* correction we determine that  $\Delta_f H^\circ_{298}(\text{CHF-CH}_3^+) < 734 \text{ kJ mol}^{-1}$ . The G2 calculation predicts an enthalpy of formation ( $684 \text{ kJ mol}^{-1}$ ) at 298 K. Note that if the dissociation is state-selective it would be expected that the thermochemical threshold lies significantly lower in energy than the experimental AE of the fragment ion, as is observed.

The  $\text{CH-CH}_2^+$  has an  $\text{AE}_{298}$  of  $15.96 \pm 0.06$  eV. This energy corresponds to that at which the signal of  $\text{CHF-CH}_3^+$  decreases, and also the onset of the  $\tilde{E}$  state of the parent ion in the TPES. The only allowed reaction is  $\text{CHF}_2\text{-CH}_3 \rightarrow \text{CH-CH}_2^+ + \text{HF} + \text{F} + e^-$ . A similar reaction has been seen in both isomers of trifluoroethane [15]. It is likely, therefore, that there is a two-step mechanism for the reaction in difluoroethane. The first step involves loss of a F atom to produce  $\text{CHF-CH}_3^+$ , the second step involves HF loss from  $\text{CHF-CH}_3^+$ . The ion yield curves of  $\text{CH-CH}_2^+$  and  $\text{CHF-CH}_3^+$  support this suggestion, because the increase in the signal of  $\text{CH-CH}_2^+$  corresponds to a decrease in the signal of  $\text{CHF-CH}_3^+$ .

### 4.3 Kinetic energy releases

Fixed-energy TPEPICO spectra were measured with improved time resolution (8ns) for ion  $\text{CF}_2\text{-CH}_3^+$ ,  $\text{CHF-CH}_3^+$  and  $\text{CHF}_2^+$  over a range of photon energies which correspond to the peaks of the TPES. In our experiments, fragment ions often have enough translation energy release from dissociation [30]. Analysis of the shapes of such TOF peaks allows a determination of the kinetic energy release distribution (KERD) and the total mean translational kinetic energy  $\langle \text{KE} \rangle_T$ , associated with a particular single-bond cleavage. The details of how to get the  $\langle \text{KE} \rangle_T$  have reported elsewhere [18, 19]. Briefly, if the fragmentation is two-bodied involving the fission of one bond only, a least-squares fitting method is applied to the peak shape of the daughter ion in order to determine the mean kinetic energy release into this ion, and then the total mean kinetic energy release,  $\langle \text{KE} \rangle_T$ , into the two fragments at a certain photon energy.

$\langle \text{KE} \rangle_T$  can be divided by the available energy,  $E_{\text{avail}}$ , to determine  $f_T$ , the fraction of the available energy been channelled into translational energy of the two fragments.  $E_{\text{avail}}$  is given by the photon energy minus the AE of the daughter ion plus thermal energy of the parent molecule at 298 K. The experimental values of  $f_T$  can then be compared with those expected if the dissociation follows a pure statistical [31] or a pure impulsive [32] model. These two limiting models are described in detail in our previous work on dissociative photoionization of  $\text{CHF}_2\text{CF}_3$  and elsewhere [13, 33]. Since some of the vibrational frequencies of the fragment ions are unknown, statistical values for  $f_T$  were calculated according to the lower limit value of  $1/(x+1)$ , where  $x$  is the number of vibrational degrees of freedom in the transition state of the unimolecular reaction [34]. Note that if dissociation follows the modified-impulsive model [35], values of  $f_T$  may be greater than those calculated for the pure-impulsive model.

High resolution TPEPICO-TOF spectrum were measured for  $\text{CHF}_2\text{-CH}_3^+ \rightarrow \text{CHF}_2^+ + \text{CH}_3 + e^-$  over several energy points which roughly corresponding the peaks on the TPES. The experimental values of  $\langle \text{KE} \rangle_T$  and  $f_T$  are derived and shown in Table 2, together with calculated values from the statistical and impulsive model. The measured values of ratio  $f_T$  are small, and suggest that a statistical mechanism might govern the C-C bond cleavage.

TPEPICO-TOF was recorded for ion  $\text{CHF-CH}_3^+$  at energy 16.10 eV. For the dissociative photoionization process  $\text{CHF}_2\text{-CH}_3^+ \rightarrow \text{CHF-CH}_3^+ + \text{F} + e^-$ , a total kinetic energy release of 1.25 eV and then the fraction ratio  $f_T$  of 0.47 were derived and listed in table 2 along with the predicted statistical and impulsive values. The agreement of the measured  $f_T$  value to that of the impulsive decay prediction probably suggests that a non-statistic mechanism dominates

the process. This behaviour seems to be common in the dissociative photoionization process of HFCs involving loss of a fluorine atom through breaking a single C-F bond. The impulsive behaviour is consistent with the molecular character largely consist of fluorine lone pair. A TPEPICO-TOF spectrum was also recorded for  $\text{CF}_2\text{-CH}_3^+$  at several photon energies. But unfavourable kinetics prevent the value of  $\langle \text{KE} \rangle_{\text{T}}$  into  $\text{CHF}_2\text{-CH}_3^+ \rightarrow \text{CF}_2\text{-CH}_3^+ + \text{H} + \text{e}^-$  from being determined accurately.

## 5. Conclusion

We have carried out a comprehensive study on the dissociative photoionisation of  $\text{CHF}_2\text{-CH}_3$  by using tunable VUV synchrotron radiation source over a wide energy range. The TPEPICO spectrum was recorded continually as a function of photon energy and ion flight time. The threshold photoelectron spectrum, ion yield curves and breakdown diagrams have been inferred. From the peak shape of time of flight mass spectrum, total mean translation kinetic energy release  $\langle \text{KE} \rangle_{\text{T}}$  and its fraction to available energy  $f_{\text{T}}$  are derived. High accurate G2 energy calculations were performed for  $\text{CHF}_2\text{-CH}_3$ ,  $\text{CHF}_2\text{-CH}_3^+$  and its fragmentation ions. The minimum energy geometry and outer valence molecular orbital of  $\text{CHF}_2\text{-CH}_3$  are computed at MP2/6-31(d) level. Combining with *ab initio* molecular orbital calculation, fragmentation process and fragmental mechanism of the valence states of parent ion are discussed. For single bond cleavage process, ion  $\text{CHF}_2^+$  seems come from statistical decay, while the kinetic energy release derived from channel  $\text{CHF}_2\text{-CH}_3^+ \rightarrow \text{CHF-CH}_3^+ + \text{F} + \text{e}^-$  shows evidence for impulsive mechanism. A two-step increase of signal  $\text{CF}_2\text{-CH}_3^+ / \text{CHF}_2\text{-CH}_2^+$  was observed, probably due to the formation of ion  $\text{CF}_2\text{-CH}_3^+ / \text{CHF}_2\text{-CH}_2^+$  through two different dissociation channels. Both computed molecular orbital character and related G2 dissociation energy support the assumption.

The ionisation threshold identified from the TPES and the appearance energies (AEs) measured from the ion yield curves are presented. Based on these AEs, new or refined upper limit values of enthalpy of formation for  $\text{CHF}_2^+$ ,  $\text{CF}_2\text{-CH}_3^+$  and  $\text{CHF-CH}_3^+$  are derived.

## Acknowledgements

We thank EPSRC for research grant, postdoctoral fellowship (WZ) and a research studentship (DJC), and the University of Birmingham for a research studentship (RYLC). WZ thank Zhejiang Normal University for a research grant.

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### ***Table captions***

**Table 1.** Energetics of dissociative photoionisation pathways of CHF<sub>2</sub>-CH<sub>3</sub>

**Table 2.** Mean translation KE releases,  $\langle KE \rangle_t$ , of the two-body fragmentation of the valence states of CHF<sub>2</sub>-CH<sub>3</sub><sup>+</sup>

### ***Figure Captions***

**Figure 1** Computed minimum energy structure of the ground state of CHF<sub>2</sub>-CH<sub>3</sub> and its three highest valence molecular orbitals. The orbitals are calculated at the MP2(full)/6-31(d) level of theory.

**Figure 2** Threshold photoelectron spectrum of CHF<sub>2</sub>-CH<sub>3</sub>. The optical resolution is 0.3 nm.

**Figure 3** Coincidence ion yields from CHF<sub>2</sub>-CH<sub>3</sub> over the energy range 12-25 eV. The optical resolution is 0.3 nm.

**Figure 4** Breakdown diagram for dissociative photoionisation of CHF<sub>2</sub>-CH<sub>3</sub>.



**Figure 1**

**Figure 2**

**Figure 3**

**Figure 4**

**Table 1**