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Threshold photoelectron–photoion coincidence study of the fragmentation of valence states of CH$_2$F–CH$_3^+$

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Abstract. We have carried out a comprehensive study of the decay dynamics of the valence electronic states of CH$_2$F–CH$_3^+$, by using threshold photoelectron–photoion coincidence (TPEPICO) spectroscopy and a tunable vacuum ultraviolet synchrotron radiation source. Threshold photoelectron spectroscopy (TPES) has been recorded for the first time in the photon energy range of $\sim$12–24 eV. Ion yield curves and breakdown diagrams have been determined in the energy range of $\sim$11.5–18 eV. The dissociation process and fragmental mechanism of the valence states of the parent ion are discussed. The mean translational kinetic energy releases for fragmentation of CH$_2$F–CH$_3^+$, via a single bond cleavage have been measured and compared with the predictions of statistical and impulsive mechanisms. For dissociation CH$_2$F–CH$_3^+$ $\rightarrow$ CHF–CH$_3^+$ + H + e$^-$, a non-statistical decay is assumed, and there seems to be a transition to statistical behaviour with increasing photon energy. For cleavage of the C–C bond to form CH$_2$F$^+$, there seems again to be a transition to statistical decay. The ionization threshold measured from the TPES and the appearance energies (AEs) identified from the ion yield curves are presented. An upper limit for the ionization threshold of CH$_2$F–CH$_3$ (11.66 $\pm$ 0.03 eV) and the enthalpy of formation of CH$_2$F–CH$_3^+$ at 298 K (679 $\pm$ 3 kJ mol$^{-1}$) are determined.

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1. Introduction

Among the group of molecules, C$_2$H$_n$F$_{6-n}$, which constitute the substituted ethane molecules, monofluoroethane is one of the potential alternative compounds to chlorofluorocarbons which deplete ozone [1]. The presence of C–H bonds will cause hydrofluorocarbons (HFCs) to react faster with the OH radical in the troposphere, thereby reducing their lifetime in the earth’s atmosphere. HFCs also lack chlorine and bromine atoms which can catalyse the removal of ozone in the stratosphere. However they still pose a threat to the environment because of their potential to contribute to global warming [2]. If the reaction of the HFC with the OH radical is sufficiently slow, the removal of these species from the atmosphere may be governed by photoionization and photodissociation processes that occur in the mesosphere. Acknowledging the vacuum-ultraviolet (VUV) photochemistry of HFCs which might take place in this region of the atmosphere is therefore important.

To date, only few papers have been published concerning the dissociative ionization and decay mechanism of valence states of CH$_2$F–CH$_3$ using VUV photoionization techniques [3]–[8]. Of these six reported works, three use either a He I or He II source [4]–[6], and one uses the method of electron impact (EI) ionization [7]. Very little work has been completed on the appearance energies (AEs) of the fragments, with only one photoionization study on the fragmentation of CH$_2$F–CH$_3$ by photoionization mass spectrometry (PIMS) leading to a determination of the AE of the fragment CH$_2$F–CH$_3^+$ [3].

As part of a series in our investigations on the fragmentation mechanism of valence electronic states of hydrofluoroethanes using threshold photoelectron–photoion coincidence (TPEPICO) spectroscopy with synchrotron radiation as a tunable VUV photoionization source, several separate investigations have been carried out on five HFCs; pentafluoroethane [9], the two isomers of tetrafluoroethane [10], and the two isomers of trifluoroethane [11]. In this paper a comprehensive study on the mechanism of valence state fragmentation of CH$_2$F–CH$_3^+$ by TPEPICO spectroscopy is presented. The threshold photoelectron spectra (TPES) and state-selected fragmentation studies of the parent ions are presented. Breakdown diagrams, yielding the formation probability of fragment 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 fragment cations have been derived or refined.

2. Theoretical and experimental method

2.1. Computation methods

Using Gaussian 2003, *ab initio* molecular orbital (MO) calculations have been carried out for CH$_2$F–CH$_3$, both in its neutral ground state and in the ground states of the parent cations. Calculations have also been performed for fragments produced by VUV dissociative photoionization (e.g. CHF–CH$_3^+$. 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-3 (G3) procedure [12]. This procedure involves single-point total energy calculations at the MP4/6-31G(d), QCISD (T)/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p), and MP2(full)/G3 large levels. In the calculations of the total electronic energies (EEs), a spin–orbit correction is added to the energies of atomic species, and a small empirical correction is employed to include the high-level correlation effects. The HF/6-31G(d) harmonic vibrational frequencies, scaled by 0.8929, are applied for zero-point vibrational energy (ZPVE) corrections to obtain the total energies at 0 K ($E_0 = EE + ZPVE$).

The enthalpies of formation at 298 K (ΔfH$_{298}$) for molecular species are calculated using the scaled HF/6-31G(d) harmonic frequencies, leading to predicted enthalpies of unimolecular reactions (e.g. CH$_2$F–CH$_3$ → CH$_2$–CH$_3^+ + F$ + e$^-$. The agreement between G3 and experimental results is usually well within ±0.13 eV (or ± 13 kJ mol$^{-1}$) [12].

2.2. Experimental methods

The TPEPICO apparatus has been described in detail elsewhere [9, 13, 14]. 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. The optical resolution employed for the experiment is 0.3 nm. Most experiments were performed using the medium-energy grating (range 150–60 nm (8–21 eV), blazed at about 90 nm). With the medium-energy grating, the measured second-order radiation is insignificant for λ < 120 nm. The wavelength of the monochromater was carefully calibrated with the known ionization potential of Ar at 15.759 and 15.937 eV, respectively. The monochromatized VUV radiation is admitted into an interaction region through a glass capillary. The photon flux is monitored, using a photomultiplier tube (PMT) attached via a sodium-salicylate-coated window behind the interaction region.

The threshold photoelectrons and positive ions produced by the VUV photoionization/fragmentation were extracted in opposite directions through a 20 V cm$^{-1}$ electric field applied across the interaction region. Threshold electrons are detected by the threshold electron analyser with an energy resolution of 10 meV [14]. Positive ions extracted from the interaction region are detected through a linear time-of-flight (TOF) mass spectrometer, pulses from the
electron and ion detectors pass through discriminator and pulse shaping circuits to a time-to-digital converter (TDC) configured in the multi-hit mode. The electron signals provide the start and the ion signals provide the stop pulses, allowing signals from the same ionization process to be detected in coincidence.

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. A cut through the histogram at fixed photon energy gives the TOF-mass spectrum (TOF-MS), which enables us to identify the fragmental ions formed in the dissociative photoionization process. A background-subtracted cut taken through the map at a fixed ion flight time corresponding to a mass peak in TOF-MS gives an ion yield curve, and several similar cuts are taken according to the produced ions. A breakdown diagram can be calculated through normalization 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 photoionization 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 [15, 16].

The gas samples of CH\(_2\)F–CH\(_3\) were obtained commercially (Fluorochem Ltd, UK) with stated purities of > 99%. They were used without further purification. The sample was injected through a needle valve. The typical operating pressure was about 5 \( \times \) 10\(^{-5}\) mbar, several orders of magnitude above the base pressure of 5 \( \times \) 10\(^{-8}\) mbar in the chamber.

### 3. Theoretical results

The minimum energy geometries of CH\(_2\)F–CH\(_3\) and CH\(_2\)F–CH\(_3\)^+ have been determined at the MP2 (full)/6-31G(d) level. Both the neutral molecule and its cation have trans structures of Cs symmetry with four atoms (H, C, C, F) lying in the symmetry plane. The main structural change after ionization is an increase of 0.37 Å in the C–C bond length, a decrease of 0.1 Å in the C–F bond length, and an increase in the \( \angle \text{FCH} \) and \( \angle \text{HCH} \) bond angles in both the CH\(_2\)F and CH\(_3\) groups. Thus, both the CH\(_2\)F and CH\(_3\) groups adopt a more planar structure upon ionization. The adiabatic ionization energy (AIE) of CHF\(_2\)–CH\(_2\)F was calculated through the G3 energy difference between the ground state of the neutral molecule and its cation. A value of 11.57 eV is then deduced.

The electronic configuration of CH\(_2\)F–CH\(_3\) (\( \tilde{X}^{1} \text{A}' \)) is \( \cdots 8(\text{A}')^2 2(\text{A}'')^2 9(\text{A}')^2 10(\text{A}')^2 3(\text{A})^2 \), where the numbering includes core orbits. The structure of the neutral molecule and the five highest valence MOs are shown in figure 1. It is difficult to give a simple characterization of these MOs due to their hybridized nature. At MP2(full)/6-31G(d) level of theory, the 3A'' highest occupied MO (HOMO) is predominantly a \( \pi^* \) orbital with a node on the symmetry plane and has mainly C–H \( \sigma \) bonding character. The orbital of next highest energy (i.e. HOMO-1), 10A' has a \( \pi^* \) antibonding contribution localized on the CH\(_2\)F group with a node perpendicular to the symmetry plane and a \( \sigma \) bonding contribution on the CH\(_3\) group. It exhibits strong C–C and C–H \( \sigma \) bonding character. The 9A' orbital (HOMO-2) is a \( \pi^* \) orbital mainly localized on
Figure 1. Computed minimum energy structure of CH$_2$F–CF$_3$($X^1$A'), and its five highest valence MOs. The orbitals are calculated at the MP2(full)/6-31(d) level of theory.

the CH$_3$ group, with strong C–H $\sigma$ bonding character and some C–F bonding contribution. Both of the next two higher excited valence orbitals (HOMO-3, HOMO-4) are $\pi^*$ orbitals with some F 2p$\pi$ lone-pair nonbonding character. The removal of an electron from this type of orbital is expected to result in C–F bond fission, i.e. fragmentation to CH$_2$–CH$_3$ + F.
4. Experimental results and discussion

4.1. TPES

The TPES of CH$_2$F–CH$_3$ was measured at an optical resolution of 0.3 nm from 11 to 24 eV over both the medium- and high-energy gratings of the Seya monochromator, as shown in figure 2. From the TPES, it can be seen that many of the states cannot be resolved. The $\tilde{X}/\tilde{A}$ state peak occurs at 12.77 ± 0.04 eV, the $\tilde{B}/\tilde{C}$ state peak occurs at 14.27 ± 0.05 eV, the $\tilde{D}$ state occurs at 16.19 ± 0.06 eV, the unresolved $\tilde{E}/\tilde{F}$ state occurs at 17.15 ± 0.07 eV, and the $\tilde{G}$ state occurs at 21.12 ± 0.08 eV. The labelling of the electronic states follows that of Yamazaki et al [5]. This TPES shows that the $\tilde{X}$ and $\tilde{A}$ states cannot be resolved in our experiment, and this observation is quite different to nearly all the HFCs that our group has studied [9]–[11], where the ground state of the parent ion is broad, but well separated in energy from the first excited electronic state. This observation is also different to the He I PES reported by Yamazaki et al [5], where the $\tilde{X}$ and $\tilde{A}$ states are resolved and peaks occur at 12.43 and 12.87 eV respectively. Note that the $ab\ initial$ calculations described in section 3 show that the energy difference between the HOMO and HOMO-1 of CH$_2$F–CH$_3$ is small, only 0.24 eV at the MP2(full)/6-31G(d) level, and the experimental result in [5] is also small, about 0.44 eV. Furthermore, there is a large geometry change after ionization, which often leads to vibrational excitation of ionic states. Thus, the fact that a broad and weak $\tilde{X}$ band overlaps partially with the $\tilde{A}$ band in the TPES of CH$_2$F–CH$_3$ and cannot be resolved is not surprising. The observation of resolved $\tilde{X}$ and $\tilde{A}$ states in the He I PES in [5] probably is that due to autoionization or a change in the relative ionization cross-section near the threshold region, as mentioned in the next paragraph, which leads to the $\tilde{X}$ state peaking higher in the He I PES than in the TPES, allowing it to be resolved from the $\tilde{A}$ state. The $\tilde{D}$ band centred around 16.19 ± 0.06 eV in the TPES of CH$_2$F–CH$_3$ is likely due to the removal of an electron from the (HOMO-4) MO which has some F 2p$\pi$ lone pair character.
When comparing the TPES recorded here with that of the He I PES obtained by Yamazaki et al. [5] the band positions agree reasonably well. The main difference between the two spectra is the relative intensity of the second band, which corresponds to the unresolved $\tilde{B}$ and $\tilde{C}$ states of the parent ion. This band is significantly more intense under threshold conditions. This could be due to either a change in the relative ionization cross-section between excitation at threshold and non-resonant He I (21.22 eV) radiation, or to autoionization effects. It is likely, as described below, that for CH$_2$F–CH$_3$ the former explanation is correct. As noted in our previous papers on small perfluorocarbons [9, 17, 18]. At each photon energy, $E$, without autoionization processes, the TPES only gives a representation of the relative photoionization cross-section under threshold conditions. But the total ion yield curve represents the total relative ionization cross-section across the energy range, from the state(s) at energy $E$ as well as from lower ionic states. These lower states release electrons of kinetic energy greater than zero. If the ionization cross-section at any particular energy is similar at threshold to that in excess of threshold where energetic electrons are released and no Rydberg states are present, then the total ionization cross-section should be equivalent to the integral of the ionization cross-section of each state, reflected in the TPES, from the onset of ionization to energy, $E$. Thus, by summing the TPES signal from threshold upward to $E$, a curve similar to that observed for the ion yield should be obtained. A comparison of the total ion yield with the integrated TPES may reveal peaks in the TPES which occur via autoionization mechanisms. The good agreement of our integrated TPES and total ion yield of CH$_2$F–CH$_3$ (figure 3) over most of the energy range, and the absence of such peaks, indicates that autoionization is not an important process here. However, at the threshold region, there is a slight discrepancy between the two curves, probably indicating the existence of Rydberg bands, as reported by Harshbarger et al. [19] and Sauvageau et al. [20].

The TPES shows that the onset of signal occurs at 11.66 ± 0.03 eV. This value is about 0.12 eV higher than that reported by Blanchette et al. [7] who studied this molecule by means of EI ionization. Due to the poor EE resolution in EI impact studies, the results obtained here should be more reliable. The calculated AIE based on the G3 method is 11.57 eV, which is smaller than the threshold electron onset, 11.66 ± 0.03 eV for CH$_2$F–CH$_3$. This discrepancy is consistent with a small Franck–Condon factor that reflects an altered conformation upon ionization. When the equilibrium geometry of the ion is very different from that of the corresponding neutral

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**Figure 3.** The total ion yield and integrated TPES of CH$_2$F–CH$_3$. 

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molecule and the lowest vibrational level is not populated in ionization by photon absorption, an overestimation of the AIE from the TPES might occur [21, 22].

4.2. Scanning energy TPEPICO experiments

A scanning energy TPEPICO spectra of CH₂F–CH₃ was measured between about 11.5 and 18 eV with an optical resolution of 0.3 nm and an ion TOF resolution of 32 ns, the medium-energy grating was used and scanned with a constant step size of 0.15 nm. Typical TOF-MS at three different energies are shown in figure 4. The parent ion CH₂F–CH₃⁺ and four fragment ions (CHF–CH₃⁺, CH₂F⁺, CH₂–CH₃⁺ and CH–CH₂⁺) were detected and their yields are shown in figure 5. From the ion yield curves, a breakdown diagram was constructed (figure 6), indicating the relative ion abundance as a function of photon energy from dissociative ionization of CH₂F–CH₃. From the ion yield curves and the breakdown diagram, it can be seen that the parent ion CH₂F–CH₃⁺ appears weakly at the lowest energy. At a slightly higher energy, the ion CHF–CH₃⁺ is observed, then CH₂F⁺ and CH₂–CH₃⁺ appear at increased energy. These four ions are the predominant ions until 15.5 eV. At higher energy, an ion of mass 27 u, CH–CH₂⁺, appears slowly and becomes the dominant ion in the range 16–18 eV.

The 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. 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. Several main ions and their AEs identified from our experiment are listed in table 1, along with the values measured from other research. The errors in the table 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 [23] to convert the observed AEs into an enthalpy of the unimolecular reaction at 298 K, Δ₁H₂⁹₈. Full details of the conversion processes are given elsewhere [9, 23]. From these AE values, the upper limits of the enthalpies of formation of ions produced from fragmentation of CH₂F–CH₃⁺ can be estimated.
the derived enthalpies of formation of these ions are listed in table 1, together with the literature values. The table shows that our results are consistent with those obtained by other groups. The enthalpies of formation ($\Delta_f H_{298}^0$) we used for all of the above calculations are taken from Chase [24] or Lias et al [25] the exception being the value for CH$_2$F–CH$_3$ [26].

Within the energy range of the unresolved $\tilde{X}$ and $\tilde{A}$ states of the parent ion, CH$_2$F–CH$_3^+$ is observed with an AE of 11.66 ± 0.03 eV. The parent ion signal is relatively weak and occurs over a narrow energy range, suggesting that this cation is weakly bound over a small range of lower vibrational levels in the Franck–Condon envelope. At a slightly higher energy, 11.90 ± 0.03 eV, a CHF–CH$_3^+$ signal appears. Using the procedure of Traeger and McLoughlin, the AE at 298 K can be converted to an upper limit of 12.02 ± 0.03 eV for $\Delta_f H_{298}^0$ for the reaction
Table 1. Energetics of dissociative photoionization pathways of CH$_2$F–CH$_3$.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Dissociation channel</th>
<th>$AE_{298}$ (eV)</th>
<th>$\Delta_{f}H_{298}$ (eV$^a$)</th>
<th>$\Delta_{f}H_{298}$ (KJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$FCH$_3^+$</td>
<td>CHF–CH$_3^+$ + H</td>
<td>11.66 ± 0.03</td>
<td>12.02 ± 0.03</td>
<td>862 ± 3</td>
</tr>
<tr>
<td>CHF$^+$</td>
<td>CH$_2$F$^+$ + CH$_3$</td>
<td>13.10 ± 0.04</td>
<td>13.25 ± 0.04</td>
<td>869 ± 4</td>
</tr>
<tr>
<td>CH$_2$–CH$_3^+$</td>
<td>CH$_2$–CH$_3^+$ + F</td>
<td>13.30 ± 0.04</td>
<td>13.40 ± 0.04</td>
<td>951 ± 4</td>
</tr>
<tr>
<td>CH–CH$_2^+$</td>
<td>CH–CH$_2^+$ + HF + H</td>
<td>14.10 ± 0.05</td>
<td>13.64</td>
<td>902$^b$</td>
</tr>
<tr>
<td></td>
<td>CH–CH$_2^+$ + F + H$_2$</td>
<td></td>
<td>15.07</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH–CH$_2^+$ + F + 2H</td>
<td></td>
<td>19.59</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The value of $\Delta_{f}H_{298}$ is derived from $AE_{298}$ of the fragment ion using the procedure of Traeger and McLoughlin [23]. For the CH–CH$_2^+$ ions, the value of $\Delta_{f}H_{298}$ is given by the enthalpy of formation of products minus that of reactants; we use values for $\Delta_{f}H_{298}$ given in [24]–[26].

$^b$Lias et al [25].

CH$_2$FCH$_3$ → CHF–CH$_3^+$ + H + e$^-$ (table 1). This fragment is the most intense and dominates up to about 15 eV. The onset of this fragment in our experiment is in excellent agreement with that observed by Williamson et al in a photoionization mass spectrometric study, 12.04 ± 0.03 eV [3].

The next fragment to appear is CH$_2$F$^+$ with an $AE_{298}$ of 13.10 ± 0.04 eV. This value can be converted into $\Delta_{f}H_{298}$ for the reaction CH$_2$FCH$_3$ → CH$_2$F$^+$ + CH$_3$ + e$^-$ to be 13.25 ± 0.04 eV (table 1). CH$_2^+$ is not observed in our experiment from C–C bond cleavage. At almost the same energy, C–F bond cleavage occurs, and the CH$_2$–CH$_3^+$ signal appears from the background at 13.30 ± 0.04 eV. This signal shows a relatively gradual rise to a maximum at approximately 15.50 eV. The onset corresponds to the unresolved $\tilde{B}$ and $\tilde{C}$ states of the parent ion.

From what has been seen so far in the ion yield curves of the ions, it is interesting to point out, unlike in the dissociative photoionization of other HFCs [9]–[11], the C–C bond does not break first at lowest energy. Note that ab inito molecular orbit calculations in this study and in Kimura and co-worker’s book [5] indicate that the 3A$^\prime$$^\prime$ orbital (HOMO) has mainly C–H bonding character. Sauvageau et al [4] studied the orbital character of CH$_2$F–CH$_3$, they also assumed that the lowest photoelectron band corresponded to ionization from an orbital of mainly C–H bonding character. That the C–H bond is stabilized more by fluorine substitution than the C–C bond is consistent with the observations here and with previous research [4, 9]–[11].

Only one ion, CH–CH$_2^+$, from multi-bond breakage is observed, having an $AE_{298}$ of 14.10 ± 0.05 eV. This corresponds to the energy at which the intensity of the CHF–CH$_3^+$ signal increases, and perhaps to the onset of the unresolved $\tilde{B}$ and $\tilde{C}$ states of the TPES. We note that a similar behaviour was observed for the threshold of the same ion, CH–CH$_2^+$, in difluoromethane [27]. For monofluoroethane, the only energetically-allowed reaction at threshold (table 1) is CH$_2$F–CH$_3$ → CH–CH$_2^+$ + HF + H + e$^-$. This process has been seen in both isomers of trifluoroethane [11] and in difluoromethane. In all these cases, therefore, the ion is likely to be produced by a two-step mechanism with common features. In monofluoroethane, the first step involves the loss of a H atom to produce CHF–CH$_3^+$, the second step (CHF–CH$_3^+$ → CH–CH$_2^+$ + HF) proceeds via HF elimination. The ion yield curves of CH–CH$_2^+$ and CHF–CH$_3^+$...
support this suggestion, because the increase in signal of CH–CH$_2$ corresponds to a decrease in signal of CHF–CH$_3$.

### 4.3. Fixed-energy TPEPICO experiments

TPEPICO-TOF spectra at a resolution of 8 ns were measured for the reactions CH$_2$F–CH$_3$ $\rightarrow$ CHF–CH$_3$ + H and CH$_2$F–CH$_3$ $\rightarrow$ CH$_2$F$^+$ + CH$_3$ over a range of photon energies which correspond to the peaks of the TPES. Fragment ions often have enough translational energy for the TOF peaks to be significantly broadened from that expected for a thermal source. The KERD and the total mean translational kinetic energy $\langle KE\rangle_T$, associated with a particular single-bond cleavage can be determined by analysis of the shapes of such TOF peaks [15, 16]. The thermal energy of the parent molecule at 298 K is convoluted into each component of the KERD, and the analysis can only apply to a two-body process with single bond fission. The details of how to get the $\langle KE\rangle_T$ have been reported elsewhere [15, 17, 18]. Briefly, if the fragmentation is two-bodied involving the fission of one bond only, a least-square 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, $\langle KE\rangle_T$, into the two fragments at a certain photon energy.

$\langle KE\rangle_T$ can be divided by the available energy, $E_{\text{avail}}$, to determine $f_T$, the fraction of the available energy 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 the 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 [28] or a pure impulsive [29] model. These two limiting models are described in detail in our previous work on dissociative photoionization of CH$_2$F–CF$_3$ and elsewhere [9, 30]. The experimental values of $\langle KE\rangle_T$ and $f_T$ are shown in table 2, together with calculated values of $f_T$ for these two models. 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 [31]. Note that if dissociation follows the modified-impulsive model [32], values of $f_T$ may be greater than those calculated for the pure-impulsive model.

For the fragment ion CHF–CH$_3$ the measured values of $\langle f\rangle_T$ show that an impulsive mechanism might govern the C–H bond cleavage. However, as the photon energy increases there seems to be a change from impulsive to statistical behaviour. We note however that the TPEPICO-TOF spectrum at 16.19 eV has a poor signal-to-noise ratio, and the fit is not robust.

TPEPICO-TOF spectra were also recorded for CH$_2$F$^+$ at two photon energies. From table 2, the measured values of $\langle f\rangle_T$ show a transition from an impulsive to a statistical mechanism as the photon energy increases. Unfortunately, the poor signal and blending of the fragments in the TPEPICO-TOF spectra prevented determination of any further $\langle KE\rangle_T$ values for CH$_2$F–CH$_3$ $\rightarrow$ CH$_2$F$^+$ + CH$_3$.

### 5. Conclusions

A comprehensive study of dissociative photoionization of CH$_2$F–CH$_3$ by TPEPICO spectroscopy over the energy ranges 12–24 eV has been performed. TPES and ion yield curves of the main fragment ions have been determined. In general, the threshold electron spectra are in good
Table 2. Mean translation KE releases, $\langle KE \rangle_T$, of the two-body fragmentation of the valence states of CH$_2$FCH$^+$$_3$.

<table>
<thead>
<tr>
<th>Parent ion</th>
<th>Fragment ion</th>
<th>$E_{hn}$ (eV)</th>
<th>$E_{avail}$ (eV)</th>
<th>$\langle KE \rangle_T$ (eV)</th>
<th>Fraction ratio exp.</th>
<th>Fraction ratio stat.</th>
<th>Fraction ratio impuls.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$F–CH$^+$$_3$</td>
<td>CHF–CH$^+$$_3$</td>
<td>12.77</td>
<td>0.89</td>
<td>0.49 ± 0.09</td>
<td>0.55 ± 0.1</td>
<td>0.06</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.27</td>
<td>2.39</td>
<td>0.67 ± 0.13</td>
<td>0.28 ± 0.06</td>
<td>0.06</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.19</td>
<td>4.31</td>
<td>0.25 ± 0.02</td>
<td>0.06 ± 0.01</td>
<td>0.06</td>
<td>0.94</td>
</tr>
<tr>
<td>CH$_2$F$^+$</td>
<td></td>
<td>13.60</td>
<td>0.35</td>
<td>0.25 ± 0.03</td>
<td>0.71 ± 0.09</td>
<td>0.06</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>14.27</td>
<td>1.02</td>
<td>0.18 ± 0.02</td>
<td>0.18 ± 0.02</td>
<td>0.06</td>
<td>0.57</td>
</tr>
</tbody>
</table>

$^a E_{avail} = E_{hn} +$ thermal energy of the parent molecule at 298 K (i.e. 0.08 eV) $- AE_{298}$ (daughter ion).

$^b$ Given by $\langle KE \rangle_T/E_{avail}$.

agreement with those of PES measured using He I radiation. The ionization threshold measured from the TPES and the AEs identified from the ion yield curves are presented, along with the corresponding reaction energies, $\Delta H^{\circ}_{298}$. A new value of the enthalpy of formation at 298 K for CHF–CH$^+$$_3$ (679 ± 3 kJ mol$^{-1}$) is determined.

High resolution TPEPICO-TOF spectra have also been measured for the dissociations which involve a single bond cleavage, with the experiment operating in the fixed-energy mode. This allowed the mean translation kinetic energy release and the fractional available energy to be derived. The experimental results lead to a full discussion of the fragmental mechanism of the valence states of CH$_2$F–CH$^+$$_3$. For the reactions CH$_2$F–CH$^+$$_3$ $\rightarrow$ CHF–CH$^+$$_3$ + H, a non-statistical decay is assumed, although as photon energy is increased there seems to be a transition to statistical behaviour. For cleavage of the C–C bond to form CH$_2$F$^+$, there seems again to be a transition to statistical decay. It was not possible to deduce unambiguously the mechanism of this reaction at higher photon energies.

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References


[27] Zhou W et al in preparation
[31] Franklin J L 1976 Science 193 725