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R.Y.L. Chim, R.A. Kennedy, R.P. Tuckett, W. Zhou, G.K. Jarvis, D.J. Collins and P.A. Hatherly

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Professor Richard Tuckett (University of Birmingham) / July 2011

# Fragmentation of energy-selected $\text{SF}_5\text{CF}_3^+$ probed by threshold photoelectron photoion coincidence spectroscopy : the bond dissociation energy of $\text{SF}_5\text{--CF}_3$ , and its atmospheric implications

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**Abstract :** Using tunable vacuum-UV radiation from a synchrotron in the range 12-26 eV, we have measured the threshold photoelectron and threshold photoelectron – photoion coincidence spectrum of  $\text{SF}_5\text{CF}_3$ , a new anthropogenic greenhouse gas. The ground state of  $\text{SF}_5\text{CF}_3^+$  is repulsive in the Franck-Condon region, the parent ion is not observed, and the onset of ionisation can only give an upper limit to the energy of the first dissociative ionisation pathway of  $\text{SF}_5\text{CF}_3$ , to  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$ . We have determined the kinetic energy released into the two fragments over a range of photon energies in the Franck-Condon region of the ground state of  $\text{SF}_5\text{CF}_3^+$ . Using an impulsive model, the data has been extrapolated to zero kinetic energy to obtain a value for the first dissociative ionisation energy for  $\text{SF}_5\text{CF}_3$  of  $12.9 \pm 0.4$  eV. A similar experiment for  $\text{CF}_4$  (to  $\text{CF}_3^+ + \text{F} + \text{e}^-$ ) and  $\text{SF}_6$  (to  $\text{SF}_5^+ + \text{F} + \text{e}^-$ ) yielded values for their dissociative ionisation energies of  $14.45 \pm 0.20$  and  $13.6 \pm 0.1$  eV, respectively, in agreement with previous data on the  $\text{CF}_3$  and  $\text{SF}_5$  free radicals. The enthalpy of formation at 0 K of  $\text{SF}_5\text{CF}_3$  is determined to be  $-1770 \pm 47$  kJ mol<sup>-1</sup>, and the dissociation energy of the  $\text{SF}_5\text{--CF}_3$  bond at 0 K to be  $392 \pm 48$  kJ mol<sup>-1</sup> or  $4.06 \pm 0.45$  eV. The implication of this bond strength is that  $\text{SF}_5\text{CF}_3$  is very unlikely to be broken down by UV radiation in the stratosphere. In addition, over the complete energy range of 12-26 eV, coincidence ion yields of  $\text{SF}_5\text{CF}_3$  have been determined.  $\text{CF}_3^+$  and  $\text{SF}_3^+$  are the most intense fragment ions, with  $\text{SF}_5^+$ ,  $\text{SF}_4^+$  and  $\text{CF}_2^+$  observed very weakly. Energetic constraints require that  $\text{SF}_3^+$ ,  $\text{SF}_4^+$  and  $\text{CF}_2^+$  can only form with  $\text{CF}_4 + \text{F}$ ,  $\text{CF}_4$  and  $\text{SF}_6$ , respectively, so that fragmentation of  $\text{SF}_5\text{CF}_3^+$  to these ions involves migration of a fluorine atom across the S–C bond.

## 1. Introduction

The greenhouse effect is usually associated with small polyatomic molecules such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{O}_3$ . The ‘natural’ greenhouse gases, mainly  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , have been responsible for hundreds of years for maintaining the temperature of the earth at *ca.* 290 K, suitable for habitation. The ‘enhanced’ greenhouse gases, mainly  $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{O}_3$ , have concentrations in the atmosphere which have increased dramatically in the last 50-100 years, have infrared (IR) absorptions where  $\text{CO}_2$  and  $\text{H}_2\text{O}$  do not absorb, and are believed to be the main culprits for global warming. It is now clear, however, that there are larger polyatomic gases of low concentrations in the atmosphere which can contribute significantly to global warming because of their exceptionally strong IR absorption in the parts of the 5-25  $\mu\text{m}$  region where other greenhouse gases do not absorb. A notable example is  $\text{SF}_6$ , which has a global warming potential (GWP) of 22,200 relative to  $\text{CO}_2$  over a time horizon of 100 years. In a very recent paper,<sup>1</sup> Sturges *et al.* have detected  $\text{SF}_5\text{CF}_3$  in the atmosphere. Previously unreported, it is believed to be anthropogenic in nature, a breakdown product of  $\text{SF}_6$  in high voltage equipment. IR absorption measurements have shown that it has the highest radiative forcing per molecule of any gas found in the atmosphere to date ( $0.57 \text{ W m}^{-2} \text{ ppb}^{-1}$ ). Antarctic firm measurements suggest that it has grown from a concentration of near zero in the late 1960s to *ca.* 0.12 parts per trillion in 1999, and stratospheric profiles suggest that the lifetime of this species in the atmosphere is between several hundred and a few thousand years. It is estimated that the GWP of  $\text{SF}_5\text{CF}_3$  is 18,000 relative to  $\text{CO}_2$ , with only  $\text{SF}_6$  having a higher value.

From an applied, atmospheric viewpoint, one of the main questions to answer is whether  $\text{SF}_5\text{CF}_3$  can be broken down by UV photodissociation in the stratosphere, or whether the loss of this species from the atmosphere is governed by bimolecular ionic reactions (*i.e.* electron attachment and ion-molecule reactions) and vacuum-UV photodissociation processes in the mesosphere. The strength of the  $\text{SF}_5\text{CF}_3$  bond is needed to answer this question. Photodissociation generally occurs through excitation of a molecule to a repulsive state. Close to the energy threshold, the cross-section for photodissociation is negligibly small. Thus,  $\text{CF}_4$  has a dissociation energy (to  $\text{CF}_3 + \text{F}$ ) of 5.61 eV,<sup>2</sup> but VUV photons with energies in excess of 12 eV are required to photodissociate  $\text{CF}_4$ .<sup>3</sup> Likewise, the bond dissociation energy of  $\text{SF}_6$  (to  $\text{SF}_5 + \text{F}$ ) is 3.82 eV,<sup>4</sup> but photodissociation is not observed until the photon energy exceeds *ca.* 10 eV.<sup>5</sup> In the lower stratosphere, the highest-energy photons have an energy of *ca.* 4.0 eV. It seems unlikely, therefore, that  $\text{SF}_5\text{CF}_3$  will be destroyed in this region through photolytic cleavage of either a C–F or a S–F bond. If the S–C bond in  $\text{SF}_5\text{CF}_3$  is relatively weak ( $< 2.5 \text{ eV}$  or  $250 \text{ kJ mol}^{-1}$ ),  $\text{SF}_5\text{CF}_3$  could, in principle, be broken down by UV photolysis. However, although an absorption spectrum has not been recorded, there is no evidence from electron energy loss spectroscopy for dissociative excited states of  $\text{SF}_5\text{CF}_3$  lying *ca.* 3-8 eV above its ground state.<sup>6</sup> If the bond strength is rather greater, then the

removal of  $\text{SF}_5\text{CF}_3$  from the atmosphere will, like  $\text{CF}_4$  and  $\text{SF}_6$ , be governed by ionic or vacuum-UV processes occurring in the mesosphere.<sup>7</sup>

We report a study of the fragmentation of the parent cation of  $\text{SF}_5\text{CF}_3$  excited by photons in the range 12–26 eV by threshold photoelectron – photoion coincidence (TPEPICO) spectroscopy. It follows on from our previous studies of  $\text{CF}_4^+$  and  $\text{SF}_6^+$ .<sup>8,9</sup> We use a technique, developed for recent work on  $\text{SeF}_6$  and  $\text{TeF}_6$  and described in Section 2,<sup>10</sup> to deduce the dissociative ionisation energy of  $\text{CF}_4$  (to  $\text{CF}_3^+ + \text{F} + \text{e}^-$ ),  $\text{SF}_6$  (to  $\text{SF}_5^+ + \text{F} + \text{e}^-$ ) and  $\text{SF}_5\text{CF}_3$  (to  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$ ) at 0 K. In this paper, these thresholds are called the *first* dissociative ionisation energies of these molecules, although we should note that the dissociation channel  $\text{SF}_5\text{CF}_3 \rightarrow \text{SF}_4^+ + \text{CF}_4 + \text{e}^-$  lies lower in energy than  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$  (Section 6). We are then able to determine the  $\text{SF}_5$ – $\text{CF}_3$  bond dissociation energy and the enthalpy of formation of  $\text{SF}_5\text{CF}_3$  at 0 K. We also report the threshold photoelectron spectrum of  $\text{SF}_5\text{CF}_3$  in the range 12–26 eV, the coincidence ion yields over this energy range, and the mean translational kinetic energy (KE) release into the fragment ions. Some indication of the dynamics of photodissociation of excited electronic states of  $\text{SF}_5\text{CF}_3^+$  can be inferred.

## 2. The first dissociative ionisation energy (DIE) of $\text{CF}_4$ , $\text{SF}_6$ and $\text{SF}_5\text{CF}_3$

The parent cations of  $\text{CF}_4$ ,  $\text{SF}_6$  and  $\text{SF}_5\text{CF}_3$  have the common property that the parent ion is not observed in a conventional 70 eV electron-impact mass spectrum.<sup>11</sup> In other words, the ground electronic state of these cations is repulsive in the Franck-Condon region, dissociating on a timescale that is very much faster than the transit time of the ion through a magnetic or quadrupole mass spectrometer. For  $\text{CF}_4^+$  and  $\text{SF}_6^+$ , it is obvious that dissociation must occur by cleavage of a C–F or S–F bond to form  $\text{CF}_3^+ + \text{F}$  or  $\text{SF}_5^+ + \text{F}$ . With  $\text{SF}_5\text{CF}_3^+$ , we assume that cleavage of the S–C bond will occur. Since the  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$  threshold lies *ca.* 0.8 eV below that of  $\text{SF}_5^+ + \text{CF}_3 + \text{e}^-$  (Section 5.2), the former products are expected to be produced from photoionisation of  $\text{SF}_5\text{CF}_3$  through the repulsive ground state of the parent cation. We define the first DIE of  $\text{CF}_4$ ,  $\text{SF}_6$  and  $\text{SF}_5\text{CF}_3$  to be the 0 K energy of  $\text{CF}_3^+ + \text{F} + \text{e}^-$ ,  $\text{SF}_5^+ + \text{F} + \text{e}^-$  and  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$  relative to the ground vibronic state of  $\text{CF}_4$ ,  $\text{SF}_6$  and  $\text{SF}_5\text{CF}_3$ , respectively.

The determination of the DIE of species whose ground state of the parent ion is repulsive in the Franck-Condon region is a notoriously difficult problem, because its value is likely to be significantly less than the energy corresponding to the onset of ionisation of the neutral precursor. Thus the photoelectron spectrum of the precursor molecule can only give an upper bound to its first DIE. This problem is well known for both  $\text{CF}_4$  and  $\text{SF}_6$ , and the DIE of these species has been the subject of controversy. The DIE of a molecule AB is given by :

$$\text{DIE (AB)} = D_0(\text{A-B}) + \text{AIE (A)} \quad (1)$$

where A–B refers to  $\text{CF}_3\text{--F}$ ,  $\text{SF}_5\text{--F}$  or  $\text{CF}_3\text{--SF}_5$ ,  $D_0(\text{A-B})$  is the dissociation energy of the A–B bond, and AIE (A) is the adiabatic ionisation energy of the A free radical. The principal unknown in the estimation of the DIE of  $\text{CF}_4$  and  $\text{SF}_6$  is the AIE of the  $\text{CF}_3$  and  $\text{SF}_5$  radicals. Whilst the  $\text{CF}_3\text{--F}$  and  $\text{SF}_5\text{--F}$  bond dissociation energies are known to an accuracy of *ca.*  $10 \text{ kJ mol}^{-1}$  or  $0.1 \text{ eV}$ ,<sup>2,4</sup> the experimental values for the AIE of the  $\text{CF}_3$  and  $\text{SF}_5$  radicals are still uncertain at the level of *ca.*  $\pm 0.3$  and  $\pm 1.0 \text{ eV}$ , respectively. The problem with  $\text{CF}_3$  arises essentially due to the change from pyramidal to planar geometry upon ionisation. A consensus has emerged that the AIE of  $\text{CF}_3$  lies between  $8.8$  and  $9.1 \text{ eV}$ ,<sup>12,13</sup> with the most complete *ab initio* calculation giving  $9.05 \text{ eV}$ .<sup>14</sup> Experimental values for the AIE of  $\text{SF}_5$  lie in the larger range  $9.6\text{--}11.5 \text{ eV}$ , a review being given in ref. 4. The consensus now is that the high values are in error, and the value of  $9.60 \pm 0.05 \text{ eV}$ <sup>4</sup> obtained from a guided ion beam study of the charge transfer reaction of  $\text{SF}_5^+$  with Xe is probably correct; the most complete *ab initio* study to date gives  $9.71 \text{ eV}$ .<sup>15</sup> For  $\text{SF}_5\text{CF}_3$ , the estimation of its first DIE needs a knowledge of both the  $\text{SF}_5\text{--CF}_3$  bond dissociation energy and the AIE of the  $\text{CF}_3$  radical. Neither is well characterised.

One method to determine the DIE of  $\text{CF}_4$ ,  $\text{SF}_6$  and  $\text{SF}_5\text{CF}_3$  directly is to use the fact that, in the Franck-Condon region, the ground state of the parent cation lies above the DIE, and perform a photoelectron – photoion coincidence experiment to measure the translational KE released into the  $\text{A}^+ + \text{B}$  fragments. From an analysis of the width and shape of the fragment ion ( $\text{A}^+$ ) time-of-flight distribution in the (T)PEPICO spectrum measured at a photon energy  $h\nu$ , it is possible to determine the kinetic energy released in fragmentation at that one energy. This will correspond to some fraction of the available energy, where

$$E_{\text{avail}} = h\nu + (\text{thermal energy of AB}) - \text{DIE(AB)} \quad (2).$$

The size of the fraction is governed by the dynamics of the decay mechanism.<sup>16</sup> The mechanism cannot unambiguously be determined from a measurement at one single photon energy. By measuring the KE release continuously as a function of photon energy, however, and assuming that the fractional KE release is independent of energy, an extrapolation to a KE release of zero gives an intercept corresponding to the DIE of AB. We used this method to determine the DIE of  $\text{SeF}_6$  and  $\text{TeF}_6$ ,<sup>10</sup> and obtained values for the 0 K enthalpy of formation of  $\text{SeF}_5^+$  and  $\text{TeF}_5^+$ . However, there were no other data with which to compare our results, so the method could not be validated. Here, we demonstrate its use to estimate the DIE of  $\text{CF}_4$  and  $\text{SF}_6$ . From the former result, we deduce the 0 K enthalpy of formation of  $\text{CF}_3^+$  and, *via*  $\Delta_f H^\circ_0(\text{CF}_3)$ ,<sup>2</sup> the AIE of  $\text{CF}_3$ . Our AIE value,  $8.84 \pm 0.20 \text{ eV}$ , is in good agreement with recent experimental

determinations<sup>12,13,17</sup> and theory.<sup>14,18</sup> The SF<sub>6</sub> result determines  $\Delta_f H^{\circ}_0$  (SF<sub>5</sub><sup>+</sup>). Using the recommended value for  $\Delta_f H^{\circ}_0$  (SF<sub>5</sub>) from the ion beam study of Fisher *et al.*,<sup>4</sup> we obtain a value for the AIE of SF<sub>5</sub> of  $9.8 \pm 0.2$  eV. This value is at the lower end of the wide range of values in the literature and, within error limits, is in agreement with the guided ion beam result.<sup>4</sup> Following these ‘test’ experiments, we have measured the first DIE of SF<sub>5</sub>CF<sub>3</sub>. Using the AIE (CF<sub>3</sub>) result above, we have been able to determine, in an indirect manner, the dissociation energy of the SF<sub>5</sub>–CF<sub>3</sub> bond.

### 3. Experimental

The apparatus for the acquisition of TPEPICO data has been described in detail elsewhere.<sup>16,19</sup> In brief, mono-energetic photons are selected using a 1 m Seya-Namioka vacuum-UV monochromator (range 40–150 nm or 8–30 eV) attached to the synchrotron storage ring at Daresbury, UK. Light enters the apparatus *via* a glass capillary, providing differential pumping between the monochromator (*ca.* 10<sup>−9</sup> Torr) and the interaction region (*ca.* 10<sup>−4</sup> Torr). The photon beam interacts with an effusive jet of sample gas, and is monitored by a photomultiplier tube *via* the visible fluorescence provided by a sodium salicylate window. A threshold electron analyser and a linear ion time-of-flight (TOF) drift tube are mounted collinearly and orthogonal to the direction of the photon beam, detecting threshold electrons and cations, respectively. The photon beam is plane-polarised, with its electric field vector also perpendicular to the direction of flight of both electrons and ions. An extraction field of 20 V cm<sup>−1</sup> draws the products of photoionisation out of the interaction region to their respective detectors. The first lens of the threshold electron analyser is designed with high chromatic aberrations, and serves to focus zero-energy electrons to the 2 mm diameter entrance aperture of a 127° post analyser. The post-analyser discriminates against energetic electrons that enter it on axis. In this configuration, the threshold analyser provides a collection efficiency of *ca.* 30 % and a resolution of 10 meV, ensuring that only zero-kinetic-energy electrons reach the channeltron electron detector. In all experiments, the resolution of the VUV monochromator was 0.3 nm, a factor of *ca.* 4–20 inferior to that of the threshold analyser, hence the resolution of these experiments is governed primarily by the monochromaticity of the photon beam. The ion TOF analyser is configured to satisfy the space-focussing condition.<sup>20</sup> It consists of two accelerating regions and a 186 mm field-free region. Ions are detected by a pair of microchannel plates arranged in the chevron configuration. The TOF resolution is sufficient to allow measurement of kinetic energy releases from photoionisation processes, whilst the analyser still maintains a high collection efficiency.

Raw signals from both the electron and ion detectors pass through discriminating and pulse-shaping circuits to a dedicated data-acquisition PC equipped with a time-to-digital converter (TDC, highest time resolution 8 ns) and a counter card. The PC also controls the scanning of the vacuum-UV monochromator. The TDC operates in the multi-hit mode, with the electrons providing the ‘start’ and the

ions the ‘stop’ pulses, and threshold electrons and ions are then detected in time-delayed coincidence. The counter card can record the threshold electron, total ion and photon flux signals. The TDC and counter card operate simultaneously, thus flux-normalised TPEPICO, threshold photoelectron, and total ion yield spectra can be measured concurrently.

Experiments can be performed as a function of VUV photon energy or at a fixed photon energy. In the scanning photon energy mode, flux-normalised TPEPICO spectra are obtained as three-dimensional histograms where the coincidence count is plotted against both the photon energy and the ion TOF. A low time resolution of the TDC, 128 ns per channel, is used, with the TOF window extending from 0 to 32.7  $\mu$ s so that all ions in the mass range 0 to *ca.* 340 u are detected. A cut through the histogram at fixed photon energies gives the TOF of the ions which are coincident with threshold electrons at those energies. Since the ion TOF is dependent only on its mass ( $\text{TOF} \propto m^{1/2}$ ) and known drift tube parameters, in most cases its identity can unambiguously be determined ; problems only arise when two possible ions differ in mass by less than 2 u,<sup>21</sup> which does not arise for the fragment ions of  $\text{SF}_5\text{CF}_3^+$ . Ion yields and breakdown diagrams as a function of photon energy may be obtained from cuts taken at fixed ion TOFs. False coincidences are removed by subtracting a cut of the same width, taken over a TOF range which differs from any of the observed ions. The monochromator is calibrated by recording the TPES of Ar through the two ... $(3s)^2(3p)^5$  ionic states of  $\text{Ar}^+$ ,  $^2\text{P}_{3/2}$  and  $^2\text{P}_{1/2}$ , at 15.759 and 15.937 eV, respectively.<sup>22</sup> For the measurement of the DIES of  $\text{CF}_4$ ,  $\text{SF}_6$  and  $\text{SF}_5\text{CF}_3$ , the TOF spectrum was recorded over a narrower time window (13.6–15.6  $\mu$ s for  $\text{CF}_3^+$ , 18.8–20.8  $\mu$ s for  $\text{SF}_5^+$ ) with a resolution of 16 ns. In the fixed photon energy mode, recorded with a TDC resolution of 16 ns, the TPEPICO spectra are two-dimensional graphs of coincidence count *vs.* ion TOF. This mode is used to measure accurate values of the total mean translational kinetic energy,  $\langle \text{KE} \rangle_t$ , for a single-bond cleavage such as the production of  $\text{CF}_3^+ + \text{SF}_5$ .

$\text{SF}_5\text{CF}_3$  was manufactured by Flura Corporation, USA (99.99 %) and used without further purification.

#### 4. Determination of the total mean translational kinetic energy release, $\langle \text{KE} \rangle_t$

The kinetic energy release distribution (KERD) and hence the total, mean translational kinetic energy release,  $\langle \text{KE} \rangle_t$ , were determined from the fragment ion peak shape obtained in the fixed photon energy experiment by the method described in detail elsewhere.<sup>21</sup> Each spectrum is fitted to a basis set of KE releases, the KERD, given by  $\varepsilon_t(n) = (2n-1)^2 \Delta E$ , with  $n=1,2,3 \dots$ .  $\Delta E$ , the minimum energy release in the basis set, depends primarily on the statistical quality of the data ; the higher the signal-to-noise ratio of the spectrum, the lower  $\Delta E$  and the higher  $n$  can be set to obtain the best fit.<sup>21</sup> The thermal energy of the parent molecule is convoluted into each component of the KERD. Each computed peak in the KERD spans the range of energies  $4(n-1)^2 \Delta E$  to  $4n^2 \Delta E$ . The reduced probability of each discrete energy,



$P[\varepsilon_t(n)]$ , is varied to minimise the least-squared errors between the simulated and experimental TOF spectra. From the derived  $P[\varepsilon_t(n)]$  vs.  $\varepsilon_t(n)$  distribution, it is simple to calculate the total mean translational KE release,  $\langle KE \rangle_t$ . The analysis assumes a two-body process, corresponding to the cleavage of one bond only, and conservation of linear momentum. This method is clearly applicable for fragmentation of  $CF_4^+$ ,  $SF_6^+$  and  $SF_5CF_3^+$  to  $CF_3^+ + F$ ,  $SF_5^+ + F$ , and  $CF_3^+ + SF_5$ , respectively, but not for three-body processes such as dissociation of  $SF_5CF_3^+$  to  $SF_3^+ + CF_4 + F$ . The analysis does not allow for anisotropy in the dissociation. The values of  $\langle KE \rangle_t$  can be compared with  $E_{avail}$  (defined in equation (2)) to determine the fraction of the available energy being channelled into translational energy of the fragments. In the experiments to determine the DIEs of  $CF_4$ ,  $SF_6$  and  $SF_5CF_3$ , this procedure is simplified by constraining  $n$  to 1, and only varying  $\Delta E$  (section 5.1). The single peak in the KERD, convoluted with the thermal energy of the parent molecule prior to ionisation, then spans the range of energies from 0 to  $4\Delta E$ , with a mean value of  $2\Delta E$ . The probability is constant within this range, zero outside. This mean value is likely to be very similar to the value of  $\langle KE \rangle_t$  obtained from the full KERD.

For a pure impulsive dissociation, applicable to the ground states of  $CF_4^+$ ,  $SF_6^+$  and  $SF_5CF_3^+$ , the release of energy occurs after the fragment ion has relaxed to its final geometry.<sup>23,24</sup> The repulsion of the atoms as the bond breaks is then so great that intramolecular collisions result between the recoiling atoms and the remainder of their recoiling fragments, and transfer of energy occurs to vibrational modes of the fragments. If the dissociation applies a torque to the fragments, rotation may also be excited. Under these circumstances,  $\langle KE \rangle_t$  and  $E_{avail}$  are related by simple kinematics :<sup>23</sup>

$$\frac{\langle KE \rangle_t}{E_{avail}} = \frac{\mu_b}{\mu_f} \quad (3)$$

where  $\mu_b$  is the reduced mass of the two atoms whose connecting bond is broken, and  $\mu_f$  is the reduced mass of the two products of the dissociation. This model was developed for dissociation of polyatomic ions to a fragment molecular ion and neutral atom,<sup>23</sup> but it is simple to show that it is valid also for a *molecular* neutral fragment. The maximum fraction of the available energy that can be channelled into translational energy of the products is predicted by this model ; for cleavage of the C–F bond in  $CF_4^+$ , S–F bond in  $SF_6^+$ , and S–C bond in  $SF_5CF_3^+$ , this fraction is 0.49, 0.72 and 0.20, respectively. The model predicts a linear dependence of  $\langle KE \rangle_t$  with  $E_{avail}$ . Within the approximation that the experimental mean value of the kinetic energy is equivalent to  $\langle KE \rangle_t$ , the DIE can be deduced by extrapolating the plot of the mean KE release vs.  $h\nu$  to a release of zero. Being a classical model, the extrapolation should be linear even for very low values of the mean KE release.

By comparison, the minimum fraction of the available energy is channelled into translation for a statistical dissociation. Klots<sup>25</sup> has then shown that, for dissociation of a parent ion to a daughter ion plus neutral atom,  $\langle KE \rangle_t$  and  $E_{\text{avail}}$  are related by :

$$E_{\text{avail}} = \frac{r-1}{2} \langle KE \rangle_t + \langle KE \rangle_t + \sum_i \frac{h\nu_i}{\exp(h\nu_i / \langle KE \rangle_t) - 1} \quad (4)$$

where  $r$  and  $\nu_i$  are the number of rotational degrees of freedom and the vibrational frequency of the  $i$ th vibrational mode of the daughter ion. Such dissociations assume that the ground electronic state of the parent ion is bound, at least in some regions of its multi-dimensional potential energy surface, and knowledge of the vibrational frequencies of the daughter ion is required. If these values are not known, it is possible to estimate a lower limit to the fractional release by :

$$\frac{\langle KE \rangle_t}{E_{\text{avail}}} = \frac{1}{x+1} \quad (5)$$

where  $x$  is the number of vibrational degrees of freedom in the transition state.<sup>26</sup> For  $\text{SF}_5\text{CF}_3^+$ ,  $x=24$ , leading to a fractional release  $> 0.04$ . From eqn (4),  $\langle KE \rangle_t$  is approximately proportional to  $E_{\text{avail}}$ . The extrapolation to zero  $\langle KE \rangle_t$ , however, is not completely linear, with a higher slope when approaching threshold as quantum effects become important. A linear extrapolation can therefore give a value for the DIE which is too low, and an underestimation of the AIE of the A radical.

## 5. Results

### 5.1 Measurement of the first dissociative ionisation energy of $\text{CF}_4$ and $\text{SF}_6$

To validate the method for determining the first DIE of  $\text{SF}_5\text{CF}_3$ , we have recorded the TPEPICO spectrum of  $\text{CF}_4$  and  $\text{SF}_6$  in the scanning photon energy mode from the onset of ionisation (*ca.* 15.5 and 15.3 eV, respectively) over the range of energies of the ground and low-lying excited states of the parent ion. For  $\text{CF}_4$ , the spectrum was recorded from 66 to 88 nm (15.5 to 18.8 eV) in 64 channels. The integrated accumulation time per wavelength channel ranged from *ca.* 20-40 minutes. This energy range encompasses the onset of ionisation of  $\text{CF}_4$  through the  $\tilde{X}^2T_1$ ,  $\tilde{A}^2T_2$  and  $\tilde{B}^2E$  states of  $\text{CF}_4^+$ . These three ionic states all dissociate to  $\text{CF}_3^+$ . The dissociation mechanism of the  $\tilde{A}^2T_2$  and  $\tilde{B}^2E$  states is uncertain.<sup>8,24</sup> However, it seems likely that the low-energy parts of the  $\tilde{X}^2T_1$  state dissociate directly in an impulsive manner from its repulsive potential energy surface to  $\text{CF}_3^+ + \text{F}$ .

Figure 1(a) shows the mean translational KE released for fragmentation to  $\text{CF}_3^+ + \text{F}$ , whilst Figure 1(b) shows the threshold photoelectron spectrum (TPES) of  $\text{CF}_4$  over the energy range 15.5 to 18.8 eV. The KE data were extracted from the multiple TOF spectra by the simplified way described in section 4. As an example, Figure 2(a) shows the TOF spectrum for  $\text{CF}_3^+$  from  $\text{CF}_4$  recorded at a photon energy of 16.05 eV, for which a mean KE release of  $0.81 \pm 0.11$  eV was obtained. A few TOF spectra were checked more rigorously by determining the full KE release distribution (Section 4), but the  $\langle \text{KE} \rangle_t$  values showed little deviation from the values shown in Figures 1(a). Values of the mean KE release range from 0.7 to 1.3 eV, with a general trend of an increasing KE release as the photon energy increases. However, the increase is not linear, suggesting that the dissociation mechanism varies for different parts of the  $\tilde{\text{X}}$ -,  $\tilde{\text{A}}$ - and  $\tilde{\text{B}}$ -state potentials of  $\text{CF}_4^+$ . There appears to be a linear increase in the KE release when  $h\nu$  corresponds to energies below the Franck-Condon maximum of each of these three states of  $\text{CF}_4^+$ . As the photon energy passes through each Franck-Condon maximum, the KE release then appears to decrease. This phenomenon is also observed in the  $\tilde{\text{X}}$ ,  $\tilde{\text{A}}$ ,  $\tilde{\text{B}}$  and  $\tilde{\text{C}}$  states of  $\text{SF}_6^+$  (see below). One explanation for this effect is that, as the photon energy is increased across a photoelectron band, symmetric vibrations are excited. If these modes do not couple efficiently to the reaction coordinate, the additional energy will not necessarily appear as an increase in the translational energy of the products. We should also note that these effects are only observed due to the high signal-to-noise ratio of the TPEPICO spectra. In particular, the spectra are superior to those of  $\text{SeF}_6^+$  and  $\text{TeF}_6^+$ ,<sup>10</sup> where no such effects were observed. Only a linear increase in the mean KE release with increasing photon energy over the range of the ground and first three excited electronic states was observed for  $\text{SeF}_6^+$  and  $\text{TeF}_6^+$ ,<sup>10</sup> with any small deviations being obscured by the limited signal-to-noise ratio of these spectra.

To deduce the DIE of  $\text{CF}_4$ , we have extrapolated the mean KE releases from only the eight lowest photon energies of Figure 1(a), since impulsive dissociation is most likely to pertain for these points. These data points lie on a straight line with a positive slope of 0.55. This value for the fractional energy release is consistent with the prediction of the pure-impulsive dissociation model, 0.49. Assuming that the decay mechanism of the  $\tilde{\text{X}}^2\text{T}_1$  state of  $\text{CF}_4^+$  does not change if it were possible to access the potential energy curve below 15.5 eV, the extrapolation of this linear region to zero KE gives the first DIE of  $\text{CF}_4$  to be  $14.45 \pm 0.20$  eV. Using enthalpies of formation at 0 K for  $\text{CF}_4$  ( $-927 \text{ kJ mol}^{-1}$ ) and  $\text{F}$  ( $+77 \text{ kJ mol}^{-1}$ ),<sup>27</sup> we determine  $\Delta_f H^0(\text{CF}_3^+)$  at 0 K to be  $390 \pm 19 \text{ kJ mol}^{-1}$ . Constraining  $\Delta_f H^0(\text{CF}_3)$  to be  $-463 \pm 4 \text{ kJ mol}^{-1}$ ,<sup>2</sup> we determine the adiabatic ionisation energy (AIE) of the  $\text{CF}_3$  radical to be  $853 \pm 19 \text{ kJ mol}^{-1}$  or  $8.84 \pm 0.20$  eV. We comment that the linear region of the graph (Fig. 1(a)) leading to the Franck-Condon maximum of the  $\tilde{\text{A}}$  state of  $\text{CF}_4^+$  also appears to extrapolate to an intercept of 14.45 eV, but with a reduced slope

A similar experiment was performed for SF<sub>6</sub> over the range 65 to 82 nm (15.1 to 19.1 eV). This energy range encompasses the  $\tilde{X}^2T_{1g}$ ,  $\tilde{A}^2T_{1u}$ ,  $\tilde{B}^2T_{2u}$  and  $\tilde{C}^2E$  states of SF<sub>6</sub><sup>+</sup>, all of which dissociate solely to SF<sub>5</sub><sup>+</sup>.<sup>8</sup> Figure 3(a) shows the mean KE measured for fragmentation to SF<sub>5</sub><sup>+</sup> + F as a function of photon energy, whilst Figure 3(b) shows the TPES of SF<sub>6</sub>. Only one isotopomer of the daughter ion (<sup>32</sup>S<sup>19</sup>F<sub>5</sub><sup>+</sup>) was used to determine the mean KE releases. As an example, Figure 2(b) shows the TOF spectrum of SF<sub>5</sub><sup>+</sup>/SF<sub>6</sub> recorded at 15.72 eV, from which a mean KE release of 0.83 ± 0.07 eV was determined. The general trend of an increasing KE release with increasing photon energy is observed but, as in CF<sub>4</sub>, the increase is not linear. Data from the eleven lowest photon energies fit to a straight line with a slope of 0.39, whereas the pure-impulsive model predicts a fractional energy release of 0.72. This discrepancy may relate to the non-planarity of the fragment SF<sub>5</sub><sup>+</sup> cation. Indeed, there is even uncertainty in the geometry of this ion, with two isomers (one square pyramidal C<sub>4v</sub>, one trigonal bipyramid D<sub>3h</sub>) predicted to have comparable energies,<sup>28</sup> although this prediction has been disputed.<sup>15,29</sup> Extrapolation to a mean KE release of zero yields the DIE of SF<sub>6</sub> to SF<sub>5</sub><sup>+</sup> + F + e<sup>-</sup> to be 13.6 ± 0.1 eV. (We comment that this value is significantly lower than a recent determination of 14.11 ± 0.08 eV from an analysis of the *maximum* peak width of SF<sub>5</sub><sup>+</sup>/SF<sub>6</sub> in a TPEPICO-TOF spectrum,<sup>30</sup> a procedure now recognised to be fraught with uncertainties.) Using the 0 K enthalpy of formation for SF<sub>6</sub> (-1206 kJ mol<sup>-1</sup>), we determine directly Δ<sub>f</sub>H<sup>0</sup><sub>0</sub> (SF<sub>5</sub><sup>+</sup>) to be 29 ± 10 kJ mol<sup>-1</sup>. Constraining Δ<sub>f</sub>H<sup>0</sup><sub>0</sub> (SF<sub>5</sub>) to the value of -915 ± 18 kJ mol<sup>-1</sup> recommended by Fisher *et al.*,<sup>4</sup> we determine the AIE of the SF<sub>5</sub> radical to be 944 ± 21 kJ mol<sup>-1</sup> or 9.8 ± 0.2 eV. Again, we note that the linear region of Figure 3(a) under the Franck-Condon maximum of the  $\tilde{A}$  state of SF<sub>6</sub><sup>+</sup> at 17.0 eV appears to extrapolate back to the same intercept of 13.6 eV.

At this stage, we comment on the assumptions and limitations of this extrapolation method. The quoted errors for CF<sub>4</sub> and SF<sub>6</sub> arise from random statistical errors in the data. Three factors, which have been ignored in our analysis, might produce systematic errors. First, if the extrapolation to zero mean KE release is not linear, an error will result in the DIE. Second, the single-value KE release determined at each photon energy from the multiple CF<sub>3</sub><sup>+</sup> or SF<sub>5</sub><sup>+</sup> TOF spectra represents a mean value; each P[ε<sub>t</sub>(n)] vs. ε<sub>t</sub>(n) distribution is constrained to n=1. Given the broad distribution of P[ε<sub>t</sub>(n)] vs. ε<sub>t</sub>(n) when each TOF spectrum is fitted to the full KE release distribution, <KE><sub>t</sub> may be slightly different from the mean KE release. Third, anisotropic effects have been observed for F-atom loss from the  $\tilde{X}^2T_{1g}$  state of SF<sub>6</sub><sup>+</sup> with β parameters ranging from 0.9 to 1.3.<sup>31</sup> Likewise, fragment ion anisotropy has been demonstrated both in the F 1s core ionisation and the valence ionisation of CF<sub>4</sub>.<sup>32,33</sup> In our experiments, the polarisation of the VUV photon beam is perpendicular to the TOF axis. The energy releases are determined from the flight times of the fragment ions, or a projection of the recoil velocity on to the TOF axis. It is therefore possible that anisotropy in the fragmentation may lead to a consistent under- or over-estimation of the

mean KE release, which could cause a small systematic error in the intercept when extrapolating these values to zero. However, this effect is difficult to quantify, and it is not even obvious whether it under- or over-estimates the DIE. Our justification for ignoring all three factors is that the enthalpies of formation at 0 K of  $\text{CF}_3^+$  and  $\text{SF}_5^+$  which we determine directly from the DIE data,  $390 \pm 19$  and  $29 \pm 10$   $\text{kJ mol}^{-1}$ , agree within experimental error with the previous best estimates, namely  $410 \pm 4$  and  $11 \pm 18$   $\text{kJ mol}^{-1}$ , respectively.<sup>2,4</sup>

## 5.2 Measurement of the first dissociative ionisation energy of $\text{SF}_5\text{CF}_3$

The onset of ionisation of  $\text{SF}_5\text{CF}_3$ , *ca.* 12.9 eV, lies significantly lower in energy than that in either  $\text{CF}_4$  or  $\text{SF}_6$ . This arises because its highest-occupied molecular orbital (HOMO) has a very different character to that of  $\text{CF}_4$  or  $\text{SF}_6$ . With  $\text{SF}_5\text{CF}_3$ , it is essentially a S–C  $\sigma$ -bonding orbital,<sup>34</sup> whereas the HOMO of both  $\text{CF}_4$  and  $\text{SF}_6$  is a F  $2p\pi$  non-bonding orbital with an ionisation energy similar to that of an isolated fluorine atom.<sup>8,35</sup> Over the range 80 to 97 nm (12.8 to 15.5 eV), which encompasses all the ground state and the lower-lying part of the first excited state of the parent cation (Figure 4(b)),  $\text{SF}_5\text{CF}_3$  dissociates exclusively to  $\text{CF}_3^+$  (see also Section 5.4). We have recorded the scanning-energy TPEPICO spectrum of  $\text{SF}_5\text{CF}_3$  over this range in 64 channels. The mean KE releases are much smaller than in  $\text{CF}_4$  and  $\text{SF}_6$ , ranging from 0.05 to 0.4 eV (Figure 4(a)). Figure 2(c) shows the TOF spectrum of  $\text{CF}_3^+/\text{SF}_5\text{CF}_3$  recorded at 14.09 eV from which a mean KE release of  $0.24 \pm 0.05$  eV was determined. Within experimental error, the 35 lowest-energy data points fit to a straight line with a slope of 0.19, in excellent agreement with the prediction of the pure-impulsive model of 0.20.<sup>23</sup> Extrapolation to a mean KE release of zero yields the first DIE of  $\text{SF}_5\text{CF}_3$  to  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$  to be  $12.9 \pm 0.4$  eV. The relatively large error in the DIE reflects the small slope of the KE release *vs.* photon energy graph, and the shallow nature of the extrapolation. We should note that the DIE, unlike that of  $\text{CF}_4$  and  $\text{SF}_6$ , is coincidentally isoenergetic with the ionisation onset of the first photoelectron band of  $\text{SF}_5\text{CF}_3$ . Two important thermochemical data can now be determined. First, using values for the 0 K enthalpies of formation of  $\text{CF}_3^+$  ( $390 \pm 19$   $\text{kJ mol}^{-1}$ ) (Section 5.1) and  $\text{SF}_5$  ( $-915 \pm 18$   $\text{kJ mol}^{-1}$ ),<sup>4</sup> we determine  $\Delta_f H^\circ_0$  ( $\text{SF}_5\text{CF}_3$ ) to be  $-1770 \pm 47$   $\text{kJ mol}^{-1}$ . This value is significantly lower than that quoted in the most recent JANAF tables,  $-1700 \pm 63$   $\text{kJ mol}^{-1}$ .<sup>27</sup> Second, using the value for AIE ( $\text{CF}_3$ ) determined in Section 5.1,  $8.84 \pm 0.20$  eV, we determine the dissociation energy of the  $\text{SF}_5$ – $\text{CF}_3$  bond at 0 K to be  $4.06 \pm 0.45$  eV or  $392 \pm 43$   $\text{kJ mol}^{-1}$ . Using the value for the AIE ( $\text{SF}_5$ ) from Fisher *et al.*,<sup>4</sup>  $9.60 \pm 0.05$  eV, the *second* DIE of  $\text{SF}_5\text{CF}_3$  (defined here to be  $\text{SF}_5^+ + \text{CF}_3 + \text{e}^-$ ) is calculated to be  $13.66 \pm 0.45$  eV. This energy is *ca.* 0.8 eV higher than the first DIE to  $\text{SF}_5 + \text{CF}_3^+ + \text{e}^-$ , and explains why only  $\text{CF}_3^+$  is observed for dissociation of the low-energy regions of the ground-state potential of  $\text{SF}_5\text{CF}_3^+$ .

### 5.3 Threshold photoelectron spectrum of SF<sub>5</sub>CF<sub>3</sub>

The threshold photoelectron spectrum (TPES) of SF<sub>5</sub>CF<sub>3</sub> was measured from 12.7 to 26.4 eV with a constant wavelength resolution of 0.3 nm (Figure 5(a)). No vibrational structure was observed. The onset of ionisation, defined as the energy at which signal is first observed above the level of background noise, is  $12.92 \pm 0.18$  eV. The vertical ionisation energy of this first band occurs at 14.13 eV. The low value of this vertical IE, *ca.* 2 eV lower than that in both CF<sub>4</sub> and SF<sub>6</sub> where the HOMO has F 2p $\pi$  non-bonding character, has already been noted. The large difference between the onset of ionisation and the vertical IE suggests a significant change in geometry between neutral and cation, probably in the S–C bond length, compatible with a repulsive ground state of the parent cation along this coordinate. *Ab initio* calculations on the structure of SF<sub>5</sub>CF<sub>3</sub> at the Hartree-Fock level predict bond angles close to either 90.0° (*e.g.* FSF) or 109.4° (*e.g.* FCS), a S–F bond length of 1.58 Å, a S–C length of 1.87 Å, and a C–F length of 1.30 Å,<sup>34</sup> in good agreement with the experimental structure from gas-phase electron diffraction.<sup>36</sup> No other structures of molecules with stoichiometry C<sub>1</sub>S<sub>1</sub>F<sub>8</sub> are stable. The HOMO of SF<sub>5</sub>CF<sub>3</sub> has a large S–C  $\sigma$ -bonding character, whereas the next three orbitals lie *ca.* 0.1 au or 2.7 eV lower in energy and are F 2p $\pi$  non-bonding in character. No minimum-energy geometry of the ground state of SF<sub>5</sub>CF<sub>3</sub><sup>+</sup> can be obtained at either the Hartree-Fock or the MP2(full)/6-31g(d) level, giving further evidence that this state is unbound.

Higher-energy peaks in the TPES are observed at 15.68, 16.94, 17.86, 19.44, 21.34, 22.01 and 24.67 eV. The broad peak at 16.94 eV, *ca.* 2.7 eV above the ground state, probably corresponds to several bands produced by removal of a F 2p $\pi$  non-bonding electron. No attempt has been made to assign the other peaks in the TPES.

### 5.4 Scanning-energy TPEPICO spectrum of SF<sub>5</sub>CF<sub>3</sub>

The TPEPICO spectrum of SF<sub>5</sub>CF<sub>3</sub> was measured from 12.7 to 26.4 eV with an optical resolution of 0.3 nm. Figure 6 shows the ions produced from the TPEPICO spectrum, summed over this range of energies. The parent ion is not observed. The five fragment ions observed are, in order of increasing mass, CF<sub>2</sub><sup>+</sup>, CF<sub>3</sub><sup>+</sup>, SF<sub>3</sub><sup>+</sup>, SF<sub>4</sub><sup>+</sup> and SF<sub>5</sub><sup>+</sup>. CF<sub>3</sub><sup>+</sup> and SF<sub>3</sub><sup>+</sup> are the dominant ions, with CF<sub>2</sub><sup>+</sup> and SF<sub>4</sub><sup>+</sup> very weak. The relative intensities of the most intense ions (CF<sub>3</sub><sup>+</sup>, SF<sub>3</sub><sup>+</sup> and SF<sub>5</sub><sup>+</sup>) are *ca.* 38:13:1, and we note that these three ions are also the most intense and formed in approximately this ratio in the 70 eV electron-impact mass spectrum of SF<sub>5</sub>CF<sub>3</sub>.<sup>11</sup> The coincident ion yields of CF<sub>3</sub><sup>+</sup> and SF<sub>3</sub><sup>+</sup> are shown in Figure 5(b). The appearance energy (AE) at 298 K of these two ions are determined to be  $12.92 \pm 0.18$  eV (for CF<sub>3</sub><sup>+</sup>) and  $14.94 \pm 0.13$  eV (for SF<sub>3</sub><sup>+</sup>). The average internal energy of SF<sub>5</sub>CF<sub>3</sub> at 298 K is calculated to be 0.17 eV,<sup>27</sup>

so this corresponds to AEs at 0 K of  $13.09 \pm 0.18$  eV ( $\text{CF}_3^+$ ) and  $15.11 \pm 0.13$  eV ( $\text{SF}_3^+$ ). The weakness of the signals for the other three fragment ions is reflected in large uncertainties in their AEs. We measure AEs at 298 K of  $13.9 \pm 1.2$ ,  $13.5 \pm 1.5$  and  $16.0 \pm 2.0$  eV for  $\text{SF}_5^+$ ,  $\text{SF}_4^+$  and  $\text{CF}_2^+$ , respectively.

The shape of the  $\text{CF}_3^+$  ion yield follows that of the TPES of  $\text{SF}_5\text{CF}_3$  from the onset of ionisation to *ca.* 20 eV, and clearly the states of the parent ion with vertical energies below 20 eV dissociate predominantly to  $\text{CF}_3^+$ . The AE at 298 K of  $\text{CF}_3^+$  corresponds to the onset of ionisation of  $\text{SF}_5\text{CF}_3$ , which is close to its first DIE to  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$ . The AE of  $\text{SF}_5^+$ , 13.9 eV with relatively large errors, also corresponds closely to the calculated second DIE of  $\text{SF}_5\text{CF}_3$  to  $\text{SF}_5^+ + \text{CF}_3 + \text{e}^-$ ,  $13.66 \pm 0.45$  eV. The  $\text{SF}_5^+$  signal is so weak that it is not possible to say whether there is any correlation between its ion yield and the electronic states of  $\text{SF}_5\text{CF}_3^+$  as revealed in the TPES. The thermochemical threshold for dissociative ionisation of  $\text{SF}_5\text{CF}_3$  to  $\text{SF}_3^+ (+\text{CF}_4 + \text{F})$  is 13.01 eV (Section 6), considerably below the observed AE at 298 K of  $\text{SF}_3^+$ ,  $14.94 \pm 0.13$  eV. In fact, this AE appears to correspond to the onset of ionisation to the  $\tilde{\text{A}}$  state of  $\text{SF}_5\text{CF}_3^+$ , indicating electronic state specificity in the fragmentation of  $\text{SF}_5\text{CF}_3^+$  to form  $\text{SF}_3^+$ . Furthermore, peaks in the  $\text{SF}_3^+$  ion yield also correlate weakly with peaks in the TPES of  $\text{SF}_5\text{CF}_3$  at 16.94, 17.86, 19.44, 21.34 and 22.01 eV. Thermochemistry shows that, at energies between threshold and 17.02 eV,  $\text{SF}_3^+$  can only form in association with the neutral products  $\text{CF}_4 + \text{F}$  (see Section 6). The ion yields of  $\text{CF}_2^+$  and  $\text{SF}_4^+$  are extremely weak. As with  $\text{SF}_5^+$ , it is not possible to say whether there is any correlation between their ion yields and peaks in the TPES of  $\text{SF}_5\text{CF}_3$ . Thermochemistry, however, shows that, certainly at low energies above threshold,  $\text{CF}_2^+$  can only form in conjunction with  $\text{SF}_6$ , and  $\text{SF}_4^+$  with  $\text{CF}_4$  (Section 6). Thus, for the three fragment ions formed involving more than one bond cleavage ( $\text{CF}_2^+$ ,  $\text{SF}_3^+$  and  $\text{SF}_4^+$ ), a fluorine migration must occur across the S–C bond to produce the necessary neutral partner(s). Such intramolecular rearrangements, involving migration of a fluorine atom across a C–X bond, have been observed in the fragmentation of perfluorocarbon cations,  $\text{C}_x\text{F}_y^+$ .<sup>37,38</sup>

## 5.5 Fixed-energy TPEPICO spectra of $\text{SF}_5\text{CF}_3$

TPEPICO-TOF spectra of  $\text{SF}_5\text{CF}_3$  were recorded at a resolution of 16 ns for the  $\text{CF}_3^+$  fragment at photon energies of 14.25, 15.69, 16.98, 17.97 and 19.07 eV, corresponding to the first five peaks in the TPES of  $\text{SF}_5\text{CF}_3$ . Accumulation times per spectrum ranged between 2 and 8 hours. Figure 7 shows the TPEPICO-TOF spectrum of  $\text{CF}_3^+/\text{SF}_5\text{CF}_3$  at an excitation energy of 14.25 eV, corresponding to the vertical ionisation energy to the ground state of the parent ion. The spectrum is fitted with  $\Delta E = 0.03$  eV,  $n = 3$ , and  $\langle \text{KE} \rangle_t$  is determined to be  $0.32 \pm 0.05$  eV (Table 1). This value of  $\langle \text{KE} \rangle_t$  corresponds to 21% of the available energy, in excellent agreement with the prediction of the pure-impulsive model.<sup>23</sup> This is to be

expected, because the ground state of  $\text{SF}_5\text{CF}_3^+$  at the Franck-Condon maximum lies over 1 eV higher in energy than the dissociative limit to  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$ . Dissociation from this repulsive potential energy surface is therefore expected to occur rapidly, probably on a sub-picosecond timescale, with a relatively large amount of the available energy released into translation of the two fragments. The  $\langle \text{KE} \rangle_t$  values determined for the other  $\text{CF}_3^+/\text{SF}_5\text{CF}_3$  spectra are shown in Table 1. As the photon energy increases from 14.25 to 19.07 eV, the values of  $\langle \text{KE} \rangle_t$  only increase by *ca.* 0.1 eV, so the fractional release into translational energy of the  $\text{CF}_3^+ + \text{SF}_5$  products decreases. It appears, therefore, that as higher-lying electronic states of  $\text{SF}_5\text{CF}_3^+$  are populated, there is a reduced coupling of the initially-excited vibrational modes to the reaction coordinate. This phenomenon, that the value of  $\langle \text{KE} \rangle_t$  does not increase as rapidly with photon energy as a pure-impulsive model would predict, has also been observed in  $\text{CF}_3^+/\text{CF}_4$  and  $\text{SF}_5^+/\text{SF}_6$ ,<sup>8</sup> and for single bond cleavages in the  $\text{CCl}_3\text{X}^+$  and  $\text{CF}_2\text{X}_2^+$  series of molecules.<sup>39,40</sup> In all these cases, the ground state of the parent cation in the Franck-Condon region lies above the first dissociative ionisation energy.

One TPEPICO-TOF spectrum was measured for  $\text{SF}_3^+$  with a resolution of 16 ns at a photon energy of 16.98 eV. The peak shape of the daughter ion fits to a KE release of  $0.17 \pm 0.01$  eV into  $\text{SF}_3^+$ . A value of  $\langle \text{KE} \rangle_t$  cannot be determined since dissociation involves more than one bond cleavage. No other fragment ions were measured as signal levels were too weak.

## 6. Thermochemistry

The 0 K energies of various dissociation channels of  $\text{SF}_5\text{CF}_3^+$  can now be determined (Table 2). We use values for the first DIE of  $\text{SF}_5\text{CF}_3$  (12.9 eV), adiabatic IEs for  $\text{CF}_3$  (8.84 eV) and  $\text{SF}_5$  (9.60 eV) determined by this work and by Fisher *et al.*<sup>4</sup> respectively, and the bond dissociation energies for  $\text{SF}_x^+ - \text{F}$  from the guided ion beam study.<sup>4</sup> The  $\text{CF}_3 - \text{F}$  bond dissociation energy (5.61 eV) is taken from Asher and Ruscic,<sup>2</sup> whilst that of  $\text{CF}_2^+ - \text{F}$  (6.32 eV) is calculated assuming an IE for  $\text{CF}_2$  of 11.44 eV.<sup>41</sup> The largest uncertainty in these energies occurs in channels involving  $\text{SF}_3^+$  and  $\text{SF}_4^+$ , at the level of *ca.* 0.3-0.5 eV. The interpretation of the mechanism of reactions which form these ions, however, does not depend on the precise values of the bond dissociation energies.

Products formed by cleavage of the S–C bond are easy to understand. As shown earlier, the onset of ionisation of  $\text{SF}_5\text{CF}_3$  at 298 K,  $12.92 \pm 0.18$  eV corresponding to  $13.1 \pm 0.2$  eV at 0 K, lies slightly higher in energy than the experimentally-deduced value for the first DIE of  $12.9 \pm 0.4$  eV. The KE releases from  $\text{SF}_5\text{CF}_3^+ \tilde{\text{X}} \rightarrow \text{CF}_3^+ + \text{SF}_5$  are therefore relatively small, making an accurate extrapolation to zero KE difficult to achieve. The calculated dissociation threshold of  $\text{SF}_5\text{CF}_3$  to  $\text{SF}_5^+ + \text{CF}_3 + \text{e}^-$ , 13.66 eV, lies



within error at the same energy as the experimentally-determined threshold of  $13.9 \pm 1.2$  eV. In other words,  $\text{SF}_5^+$  turns on, albeit very weakly, at its thermochemical threshold. For photon energies above this threshold, dissociation to  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$  dominates that to  $\text{CF}_3 + \text{SF}_5^+ + \text{e}^-$ . This effect has also been observed for reactions of cations with recombination energies in excess of 13.66 eV with  $\text{SF}_5\text{CF}_3$ , where the  $\text{CF}_3^+$  product dominates  $\text{SF}_5^+$ .<sup>42</sup>

Channels involving more complicated photodissociation processes are perhaps more interesting. The threshold for production of  $\text{SF}_3^+$  at 298 K is measured to be  $14.94 \pm 0.13$  eV. This threshold corresponds to the onset of ionisation to the second band in the TPES of  $\text{SF}_5\text{CF}_3$ , and suggests a non-statistical electronic state-selective fragmentation of the  $\tilde{\text{A}}$  state of  $\text{SF}_5\text{CF}_3^+$  is occurring. Even allowing for a significant uncertainty in the enthalpy of formation of  $\text{SF}_3^+$ , it is clear from Table 2 that this channel is energetically only open if  $\text{SF}_3^+$  forms in conjunction with  $\text{CF}_4 + \text{F} + \text{e}^-$  (dissociation energy 13.01 eV).  $\text{SF}_3^+$  cannot form with  $\text{CF}_3$  and either  $\text{F}_2$  or  $2\text{F}$ , since these channels lie *ca.* 2.1 or 3.7 eV above the experimentally-determined AE of  $\text{SF}_3^+$ . Likewise,  $\text{SF}_4^+$  and  $\text{CF}_2^+$  form very weakly with AEs of 13.5 and 16.0 eV. Table 2 shows that  $\text{SF}_4^+$  can only form with  $\text{CF}_4$ , and  $\text{CF}_2^+$  with  $\text{SF}_6$  at energies close to their respective thresholds. Thus, all these three fragmentation channels must involve a fluorine atom migration across the S–C bond to form the requisite neutral partner.

## 7. Discussion

The TPEPICO data in both the scanning photon and the fixed photon energy modes have been discussed in Sections 5.4 and 5.5. Here, we discuss only the results to deduce the dissociative ionisation energy of  $\text{CF}_4$ ,  $\text{SF}_6$  and  $\text{SF}_5\text{CF}_3$ . The value of the AIE of the  $\text{CF}_3$  radical, and hence the DIE of  $\text{CF}_4$ , has been controversial for many years. As described in section 2, the difficulty in measuring accurately the AIE of  $\text{CF}_3$  arises because of the change in geometry between the neutral (pyramidal,  $\text{C}_{3v}$ ) and ionised (planar,  $\text{D}_{3h}$ ) forms of the radical, resulting in a negligibly-small Franck-Condon overlap factor at threshold.<sup>18</sup> The experimental data up to 1998 were reviewed,<sup>12</sup> and an upper limit of  $8.8 \pm 0.2$  eV for the AIE of  $\text{CF}_3$  was recommended. Since then, a new *ab initio* calculation<sup>14</sup> and further photoionisation experiments on  $\text{CF}_3\text{Br} \rightarrow \text{CF}_3^+ + \text{Br} + \text{e}^-$ <sup>17</sup> both suggest that the AIE ( $\text{CF}_3$ ) is somewhat higher, between 9.0 and 9.1 eV. In addition, Irikura<sup>13</sup> has suggested that some of the low values of the AIE (<8.6 eV) from ion-molecule chemical reactions may be in doubt, because entropy effects have been ignored in determining whether such reactions may proceed at a reasonable rate. Our result does not add significantly to this controversy. However, it is gratifying that the extrapolation method (Figure 1(a)) gives a value for the DIE of  $\text{CF}_4$ ,  $14.45 \pm 0.20$  eV, which leads to a value for the AIE of the  $\text{CF}_3$  radical,  $8.84 \pm 0.20$  eV, which is consistent with the recommendations of two recent reviews.<sup>12,13</sup> It seems unlikely that this method will

ever be able to give an accuracy in the DIE better than *ca.*  $\pm 0.1$  eV, when an extrapolation of over 1 eV, as here, is involved.

The range of values in the recent literature for the AIE of the SF<sub>5</sub> radical is even greater, with values spanning *ca.* 9.6 to 11.5 eV.<sup>4</sup> The lowest value of  $9.60 \pm 0.05$  eV, and probably the most reliable because it is a *direct* measurement, comes from a guided ion beam mass spectrometric study.<sup>4</sup> Both our new value for the first DIE of SF<sub>6</sub>,  $13.6 \pm 0.1$  eV, and that derived for the AIE of SF<sub>5</sub>,  $9.8 \pm 0.2$  eV, are in excellent agreement with the results of Fisher *et al.*<sup>4</sup> The AIE result is also in good agreement with two independent Gaussian-2 *ab initio* calculations.<sup>15,43</sup> All three values are slightly higher than that calculated, 9.52 eV, at the CCSD(T) level of theory.<sup>44</sup>

The purpose of these CF<sub>4</sub> and SF<sub>6</sub> experiments was *not* to measure new values for the ionisation energies of the CF<sub>3</sub> and SF<sub>5</sub> radicals, but rather to validate the extrapolation method described in Section 2. The results show that this has been achieved. Within the limitations of this method described in section 5.1, we therefore have confidence in the KE extrapolation data for SF<sub>5</sub>CF<sub>3</sub> (Figure 4(a)), and the determination of its first DIE to CF<sub>3</sub><sup>+</sup> + SF<sub>5</sub> + e<sup>-</sup>. From this value, we have been able to determine the 0 K enthalpy of formation of SF<sub>5</sub>CF<sub>3</sub> and D<sub>0</sub>(SF<sub>5</sub>-CF<sub>3</sub>). The strength of the SF<sub>5</sub>-CF<sub>3</sub> bond,  $4.06 \pm 0.45$  eV, is slightly greater than that of the SF<sub>5</sub>-F bond in SF<sub>6</sub>, 3.82 eV.<sup>4</sup> The atmospheric implication of this measurement is that SF<sub>5</sub>CF<sub>3</sub>, like SF<sub>6</sub> and CF<sub>4</sub>, is very unlikely to be broken down by UV radiation in the stratosphere. Also like CF<sub>4</sub> and SF<sub>6</sub>,<sup>7</sup> the reactions of O (<sup>1</sup>D) and the OH radical with SF<sub>5</sub>CF<sub>3</sub> are likely to be very slow. Taken together, these data are consistent with the observed atmospheric profile of SF<sub>5</sub>CF<sub>3</sub> in the stratosphere, which has been interpreted to indicate a lifetime of the order of one thousand years.<sup>1</sup> Its removal from the atmosphere is likely to be determined by ionic processes (*i.e.* electron attachment and ion-molecule reactions) and possibly VUV photodissociation with Lyman- $\alpha$  radiation occurring in the mesosphere. The rate constant for electron attachment to SF<sub>5</sub>CF<sub>3</sub> at room temperature in a Swarm apparatus has recently been measured.<sup>45</sup> Its value suggests a lifetime of SF<sub>5</sub>CF<sub>3</sub> in the atmosphere of less than 1000 years.

## 8. Conclusions

Using tunable VUV radiation from a synchrotron source and threshold photoion-photoelectron coincidence spectroscopy, we have studied the fragmentation of the valence states of SF<sub>5</sub>CF<sub>3</sub><sup>+</sup> over the energy range 12 to 26 eV. Threshold electron spectra and coincidence ion yields have been recorded with the experiment operating in the scanning photon energy mode. CF<sub>3</sub><sup>+</sup> is the most intense fragment ion over this range of energies, and its ion yield follows that of the TPES of SF<sub>5</sub>CF<sub>3</sub> from *ca.* 12-20 eV. SF<sub>3</sub><sup>+</sup> is the second most intense fragment ion. Its yield shows some evidence for state-selective fragmentation.

The ion yields of  $\text{SF}_5^+$ ,  $\text{SF}_4^+$  and  $\text{CF}_2^+$  are weak.  $\text{SF}_5^+$  turns on at the thermochemical dissociation energy of  $\text{SF}_5^+ + \text{CF}_3 + \text{e}^-$ . Like  $\text{SF}_3^+$ ,  $\text{SF}_4^+$  and  $\text{CF}_2^+$  turn on at energies which are only compatible with the lowest-energy dissociation channel involving that ion. Thus  $\text{SF}_3^+$  can only form in conjunction with  $\text{CF}_4 + \text{F} + \text{e}^-$ ,  $\text{SF}_4^+$  with  $\text{CF}_4 + \text{e}^-$ , and  $\text{CF}_2^+$  with  $\text{SF}_6 + \text{e}^-$ . In all cases, a fluorine atom must migrate across the S–C bond.

In the fixed photon energy mode, the translational kinetic energy released into  $\text{CF}_3^+ + \text{SF}_5$  has been measured at five different excitation energies over the range 14 to 19 eV. The values of  $\langle \text{KE} \rangle_t$  range from 0.29 to 0.40 eV. Whereas dissociation of the ground state of  $\text{SF}_5\text{CF}_3^+$  appears to follow a pure-impulsive model with a fractional release into translational energy of 0.19, that from excited states shows a lower fractional release. This phenomenon has been observed in other molecules (*e.g.*  $\text{CF}_4$  and  $\text{SF}_6$ ),<sup>8</sup> where the ground state of the parent ion in the Franck-Condon region lies above the first DIE.

We have also used the scanning photon energy TPEPICO experiment to deduce the first DIE of  $\text{CF}_4$  (to  $\text{CF}_3^+ + \text{F} + \text{e}^-$ ),  $\text{SF}_6$  (to  $\text{SF}_5^+ + \text{F} + \text{e}^-$ ), and  $\text{SF}_5\text{CF}_3$  (to  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$ ), obtaining values of  $14.45 \pm 0.20$ ,  $13.6 \pm 0.1$ , and  $12.9 \pm 0.4$  eV, respectively. From the first two results, we determine values for the adiabatic IE of the  $\text{CF}_3$  and  $\text{SF}_5$  free radicals to be  $8.84 \pm 0.20$  and  $9.8 \pm 0.2$  eV, respectively. These results are in good agreement with what we believe to be the most reliable values in the recent literature. The fractional kinetic energy release from  $\text{SF}_6^+ \rightarrow \text{SF}_5^+ + \text{F}$  is significantly less than that predicted by the pure-impulsive model,<sup>23</sup> whereas that from  $\text{CF}_4^+$  or  $\text{SF}_5\text{CF}_3^+ \rightarrow \text{CF}_3^+ + \text{F}$  or  $\text{SF}_5$  is in good agreement with this model. This result may relate to uncertainty in the geometry of  $\text{SF}_5^+$ .<sup>28</sup> From the first DIE of  $\text{SF}_5\text{CF}_3$ , we are able to determine the enthalpy of formation at 0 K of  $\text{SF}_5\text{CF}_3$  ( $-1770 \pm 47$  kJ mol<sup>-1</sup>) and the dissociation energy of the  $\text{SF}_5$ – $\text{CF}_3$  bond at 0 K ( $4.06 \pm 0.45$  eV). These errors are dominated by the uncertainty in the first DIE of  $\text{SF}_5\text{CF}_3$ . The new value for the enthalpy of formation of  $\text{SF}_5\text{CF}_3$  is 70 kJ mol<sup>-1</sup> lower than that given in the JANAF tables.<sup>27</sup> Its value has already been used to determine possible product channels for reactions of small atmospheric cations (*e.g.*  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{O}_2^+$ ) with  $\text{SF}_5\text{CF}_3$ .<sup>42</sup> This type of reaction is just one of several bimolecular processes which could remove this molecule from the atmosphere. Indeed, the electron attachment data strongly suggest that dissociative electron attachment is the dominant removal process.<sup>45</sup>

The high value of the  $\text{SF}_5$ – $\text{CF}_3$  bond dissociation energy suggests that it is unlikely to be broken down by UV photodissociation in the stratosphere. Furthermore, from a low-resolution electron energy loss spectrum (*i.e.* a pseudo VUV absorption spectrum),<sup>6</sup> there is no evidence for excited states of  $\text{SF}_5\text{CF}_3$  lying *ca.* 3–8 eV above its ground state with appreciable absorption cross-sections. If photon-induced processes dominate the removal of  $\text{SF}_5\text{CF}_3$  from the earth's atmosphere, vacuum-UV photodissociation

with Lyman- $\alpha$  radiation in the mesosphere seems more likely. We suggest that measurement of the absorption cross-section of SF<sub>5</sub>CF<sub>3</sub> at 121.6 nm, similar to that made for CF<sub>4</sub> and SF<sub>6</sub>,<sup>7</sup> would be useful additional data in determining more accurately the lifetime of SF<sub>5</sub>CF<sub>3</sub> in the atmosphere.

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**Table 1.** Total mean translational kinetic energy release,  $\langle \text{KE} \rangle_t$ , of the two-body fragmentation of the valence states of  $\text{SF}_5\text{CF}_3^+$

Parent ion	Daughter ion	E / eV	$E_{\text{avail}} / \text{eV}^a$	$\langle \text{KE} \rangle_t / \text{eV}$	$\langle f \rangle_{t, \text{exp}}^b$	$\langle f \rangle_{t, \text{stat}}$	$\langle f \rangle_{t, \text{imp}}$
$\text{SF}_5\text{CF}_3^+$	$\text{CF}_3^+$	19.07	6.34	$0.37 \pm 0.01$	0.06	0.04	0.20
	$\text{CF}_3^+$	17.97	5.24	$0.40 \pm 0.01$	0.08	0.04	0.20
	$\text{CF}_3^+$	16.98	4.25	$0.38 \pm 0.01$	0.09	0.04	0.20
	$\text{CF}_3^+$	15.69	2.96	$0.29 \pm 0.02$	0.10	0.04	0.20
	$\text{CF}_3^+$	14.25	1.52	$0.32 \pm 0.05$	0.21	0.04	0.20
$\text{SF}_5\text{CF}_3^+$	$\text{SF}_3^+$	16.98 <sup>c</sup>					

<sup>a</sup>  $E_{\text{avail}}$  is defined in equation (2)

<sup>b</sup> Given by  $\langle \text{KE} \rangle_t / E_{\text{avail}}$

<sup>c</sup> The peak shape of the  $\text{SF}_3^+$  daughter ion at this photon energy fits to a mean KE release of  $0.17 \pm 0.01$  eV.

**Table 2.** Energetics of important dissociation channels and ionisation energies of  $\text{SF}_5\text{CF}_3$ .

Neutral / parent ion	Dissociation channel	Dissociation energy / eV <sup>a</sup>	Vertical ionisation energy / eV
$\text{SF}_5\text{CF}_3^+ \tilde{\text{G}}$			24.67
$\text{SF}_5\text{CF}_3^+ \tilde{\text{F}}$			22.01
$\text{SF}_5\text{CF}_3^+ \tilde{\text{E}}$			21.34
$\text{SF}_5\text{CF}_3^+ \tilde{\text{D}}$			19.44
	$\text{CF}_3^+ + \text{SF}_3 + 2\text{F} + \text{e}^-$	19.28	
	$\text{CF}_2^+ + \text{SF}_5 + \text{F} + \text{e}^-$	19.22	
	$\text{SF}_3^+ + \text{CF}_3 + 2\text{F} + \text{e}^-$	18.62	
	$\text{SF}_4^+ + \text{CF}_3 + \text{F} + \text{e}^-$	18.26	
$\text{SF}_5\text{CF}_3^+ \tilde{\text{C}}$			17.86
	$\text{SF}_5^+ + \text{CF}_2 + \text{F} + \text{e}^-$	17.37	
	$\text{SF}_3^+ + \text{CF}_3 + \text{F}_2 + \text{e}^-$	17.02	
$\text{SF}_5\text{CF}_3^+ \tilde{\text{B}}$			16.94
$\text{SF}_5\text{CF}_3^+ \tilde{\text{A}}$			15.68
	$\text{CF}_3^+ + \text{SF}_4 + \text{F} + \text{e}^-$	15.41	
	$\text{CF}_2^+ + \text{SF}_6 + \text{e}^-$	15.40	
$\text{SF}_5\text{CF}_3^+ \tilde{\text{X}}$			14.13
	$\text{SF}_5^+ + \text{CF}_3 + \text{e}^-$	13.66	
	$\text{SF}_3^+ + \text{CF}_4 + \text{F} + \text{e}^-$	13.01	
	$\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$	12.90	
	$\text{SF}_4^+ + \text{CF}_4 + \text{e}^-$	12.65	
	$\text{SF}_5 + \text{CF}_3$	4.06	
$\text{SF}_5\text{CF}_3 \tilde{\text{X}}$			0

<sup>a</sup> Dissociation energies of channels involving  $\text{CF}_3^+$  and  $\text{SF}_x^+$  ( $x=3-5$ ) are calculated from the experimental DIE of  $\text{SF}_5\text{CF}_3$  to  $\text{CF}_3^+ + \text{SF}_5 + \text{e}^-$  (12.9 eV), bond dissociation energies at 0 K of  $\text{SF}_x^+$  from Fisher *et al.*,<sup>4</sup> adiabatic IEs for  $\text{CF}_3$  and  $\text{SF}_5$  of 8.84 and 9.60 eV (see text), and a bond dissociation energy for  $\text{CF}_3\text{--F}$  of 5.61 eV.<sup>2</sup> Channels involving  $\text{CF}_2^+$  are calculated using an enthalpy of formation for this ion of 922 kJ mol<sup>-1</sup>.<sup>41</sup>



## FIGURE CAPTIONS

**Figure 1** (a) Mean total kinetic energy released in the reaction  $\text{CF}_4 + h\nu \rightarrow \text{CF}_3^+ + \text{F} + \text{e}^-$  for photon energies in the range 15.5 to 18.8 eV. A linear extrapolation to zero kinetic energy gives the dissociative ionisation energy of  $\text{CF}_4$ ,  $14.45 \pm 0.20$  eV. The error in each value of the kinetic energy release is *ca.* 20 %. (b) Threshold photoelectron spectrum of  $\text{CF}_4$  over the same range of energies.

**Figure 2** TPEPICO-TOF spectra (open circles) for (a)  $\text{CF}_3^+/\text{CF}_4$ , (b)  $\text{SF}_5^+/\text{SF}_6$  and (c)  $\text{CF}_3^+/\text{SF}_5\text{CF}_3$  recorded at photon energies of 16.05, 15.72 and 14.09 eV, respectively. Shown as solid lines, the data fit to mean kinetic energy releases of  $0.81 \pm 0.11$ ,  $0.83 \pm 0.07$  and  $0.24 \pm 0.05$  eV, respectively (see text).

**Figure 3** (a) Mean total kinetic energy released in the reaction  $\text{SF}_6 + h\nu \rightarrow \text{SF}_5^+ + \text{F} + \text{e}^-$  for photon energies in the range 15.1 to 19.1 eV. A linear extrapolation to zero kinetic energy gives the dissociative ionisation energy of  $\text{SF}_6$ ,  $13.6 \pm 0.1$  eV. The error in each value of the kinetic energy release is *ca.* 20 %. (b) Threshold photoelectron spectrum of  $\text{SF}_6$  over the same range of energies.

**Figure 4** (a) Mean total kinetic energy released in the reaction  $\text{SF}_5\text{CF}_3 + h\nu \rightarrow \text{CF}_3^+ + \text{SF}_5 + \text{e}^-$  for photon energies in the range 13.3 to 15.5 eV. A linear extrapolation to zero kinetic energy gives the first dissociative ionisation energy of  $\text{SF}_5\text{CF}_3$ ,  $12.9 \pm 0.4$  eV. The error in each value of the kinetic energy release is *ca.* 20 %. (b) Threshold photoelectron spectrum of  $\text{SF}_5\text{CF}_3$  over the same range of energies.

**Figure 5** (a) Threshold photoelectron spectrum of  $\text{SF}_5\text{CF}_3$  at a resolution of 0.3 nm. The electronic states of the parent cation are labelled  $\tilde{\text{X}}$  through  $\tilde{\text{G}}$  (Table 2). (b) Coincidence ion yields of  $\text{CF}_3^+$  and  $\text{SF}_3^+$ , the two most intense fragment ions.

**Figure 6** Time-of-flight spectrum of the fragment ions from  $\text{SF}_5\text{CF}_3$ , summed over the photoexcitation energies 12.7 to 26.4 eV.

**Figure 7** (a) Coincidence TOF spectrum (dots) of  $\text{CF}_3^+$  from  $\text{SF}_5\text{CF}_3$  photoionised at 14.25 eV into the ground,  $\tilde{\text{X}}$  state of the parent cation. The solid line gives the best fit to the data, comprised of three contributions ( $n=1-3$ ) in the basis set for  $\epsilon_t(n)$ . The reduced probability of each contribution is shown in (b). The fit yields a total mean translational kinetic energy into  $\text{CF}_3^+ + \text{SF}_5$  of  $0.32 \pm 0.05$  eV which constitutes 21 % of the available energy.

Figure 1

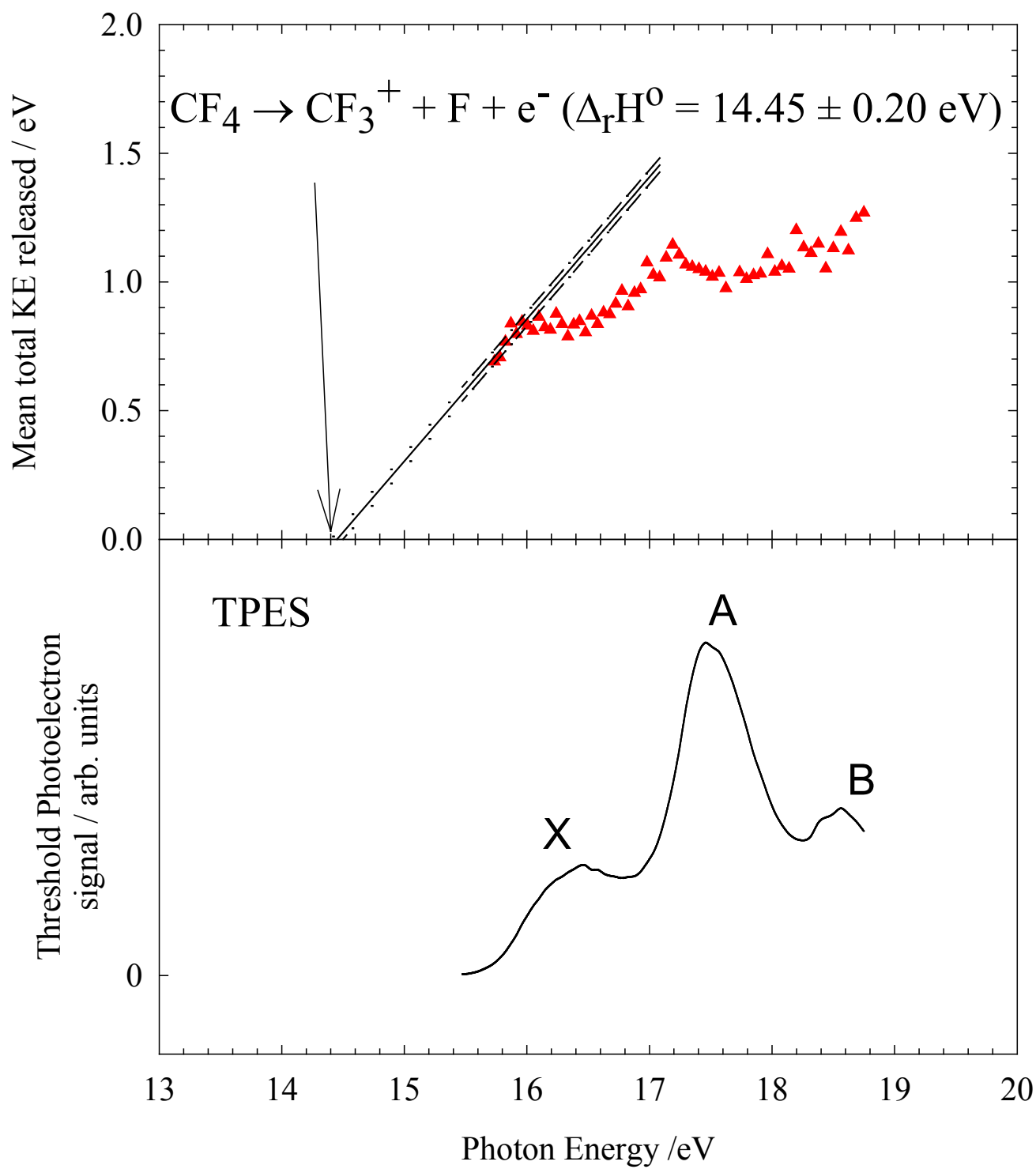


Figure 2

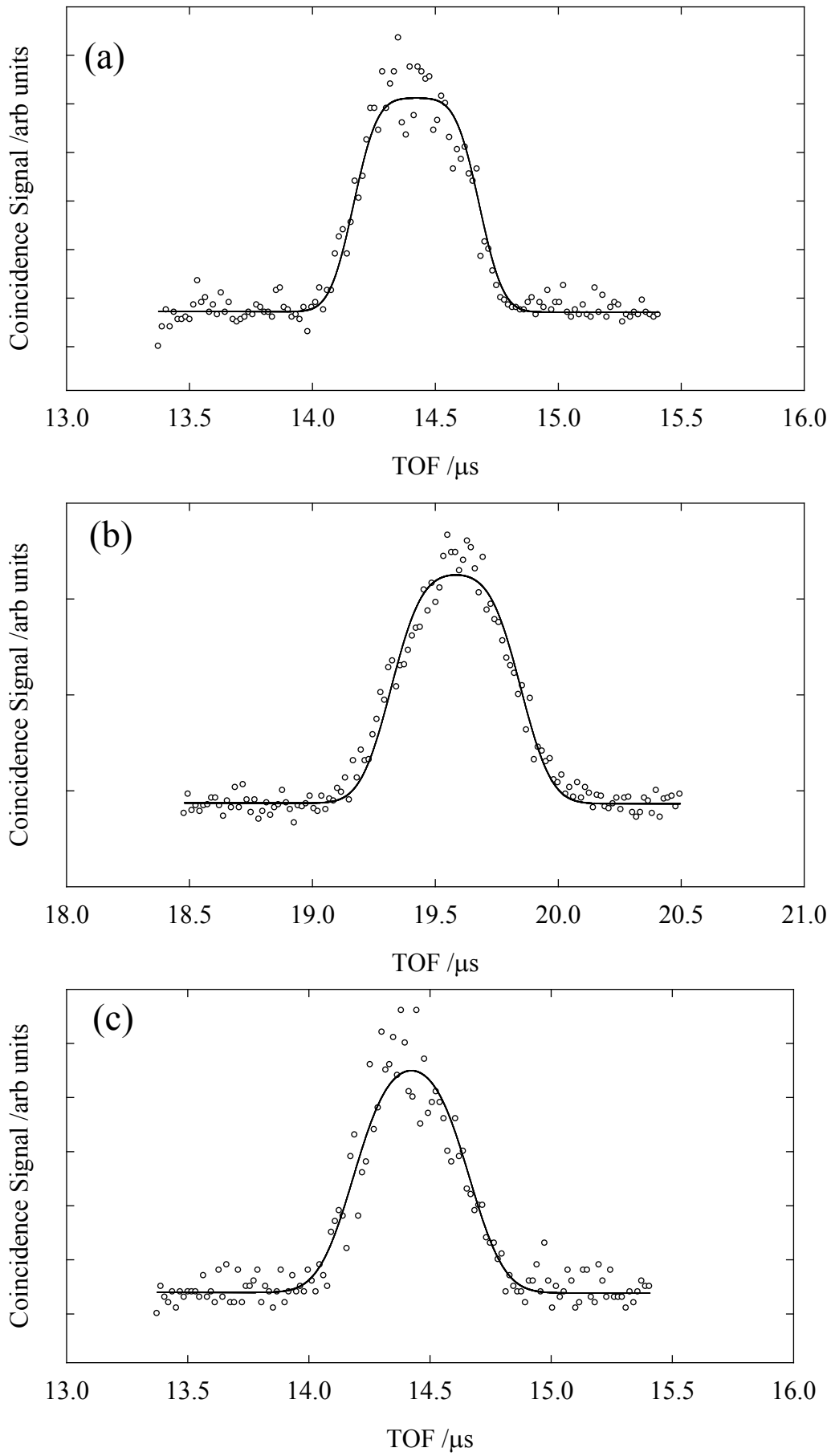


Figure 3

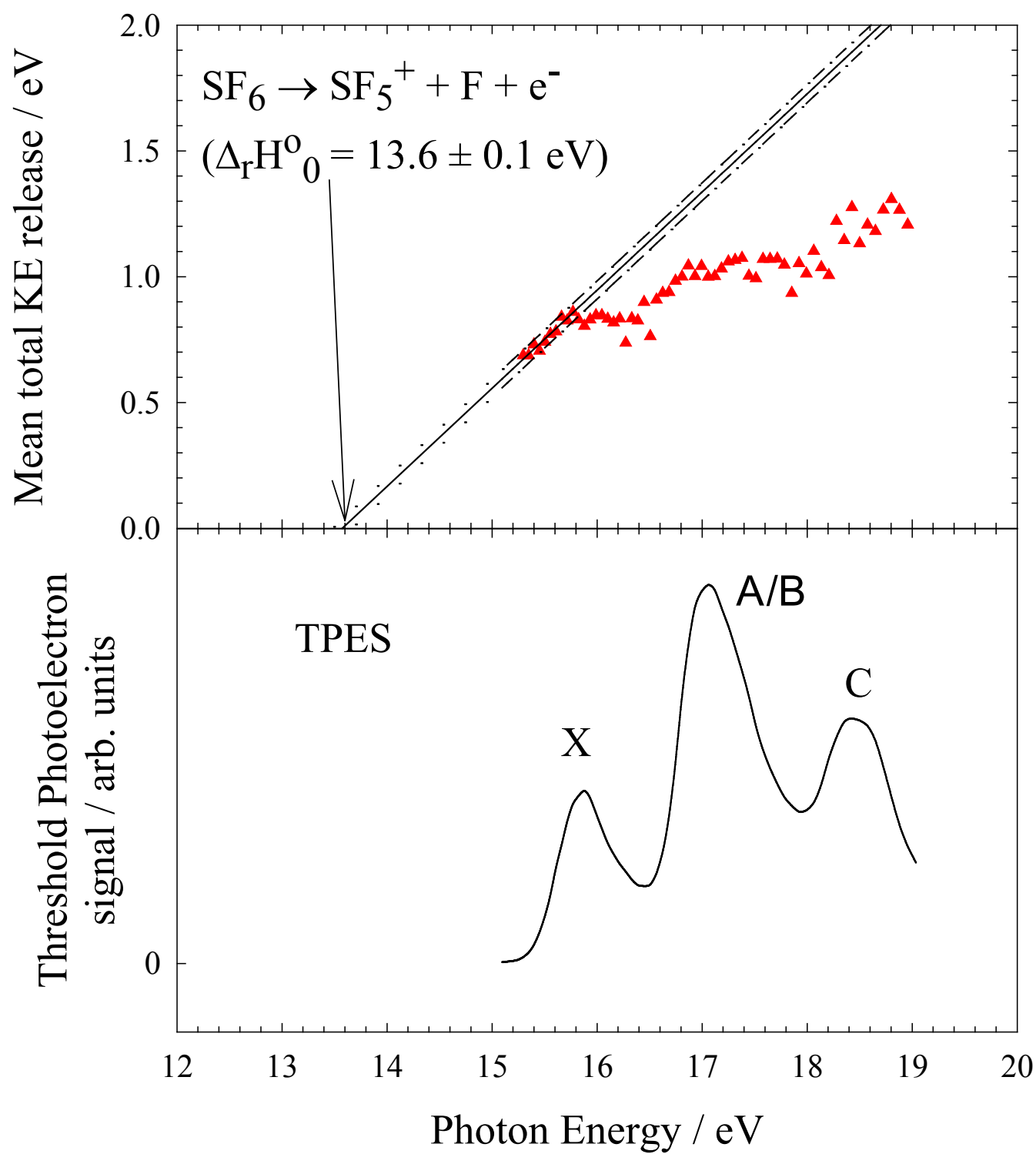


Figure 4

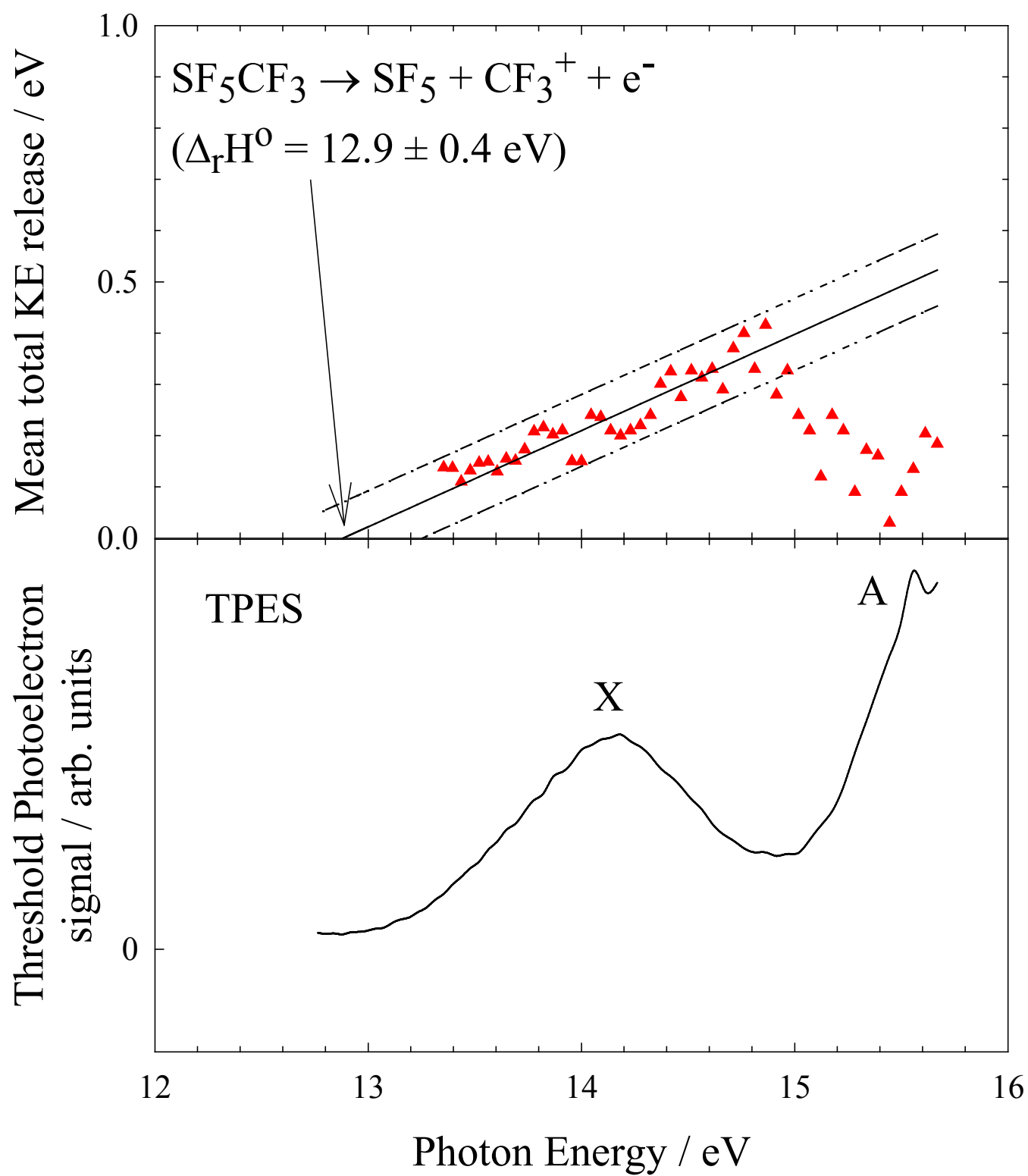


Figure 5

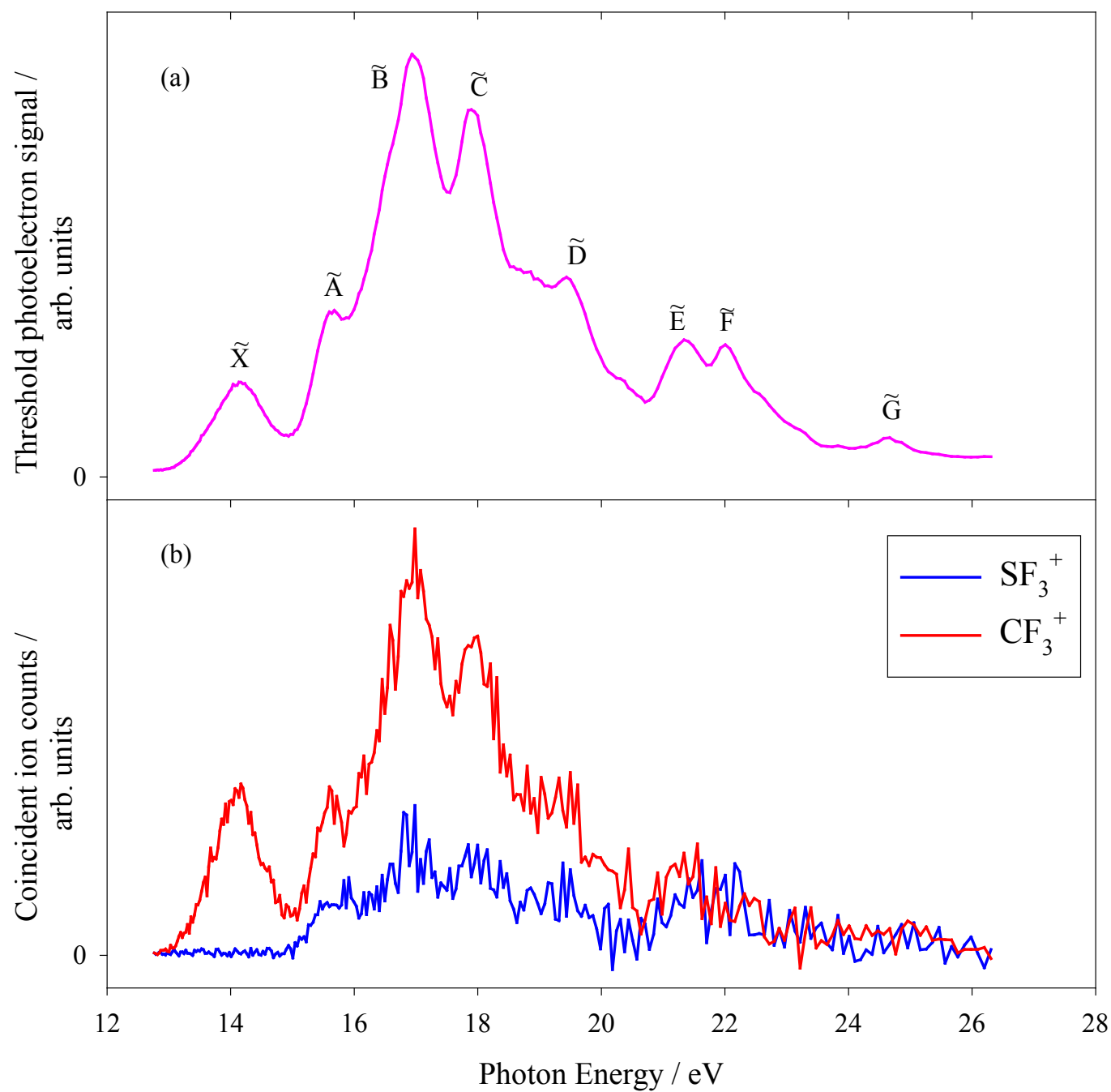


Figure 6

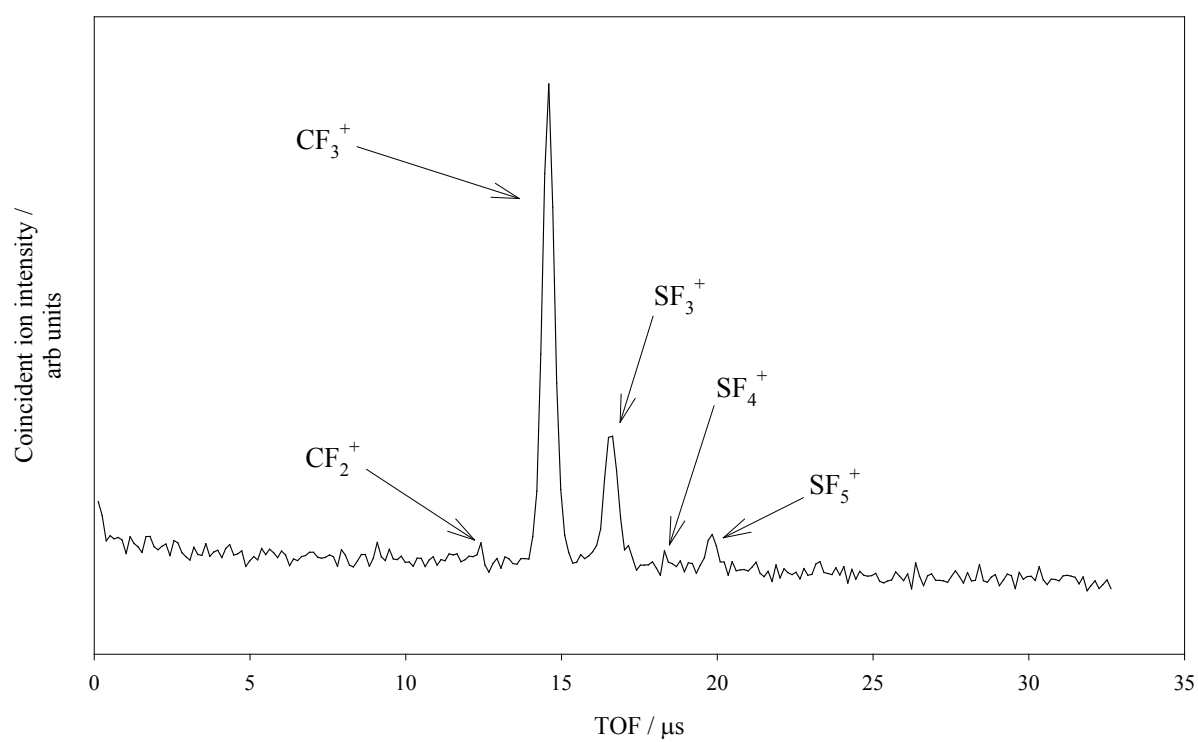


Figure 7

