

# Fragmentation of the valence electronic states of SeF<sub>6</sub><sup>+</sup> and TeF<sub>6</sub><sup>+</sup> studied by threshold photoelectron-photoion coincidence spectroscopy

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## Fragmentation of the valence electronic states of $\text{SeF}_6^+$ and $\text{TeF}_6^+$ studied by threshold photoelectron-photoion coincidence spectroscopy

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### Abstract

Threshold photoelectron-photoion coincidence (TPEPICO) spectroscopy has been performed on  $\text{SeF}_6$  and  $\text{TeF}_6$  and breakdown diagrams constructed. The ground electronic states of  $\text{XF}_6^+$  ( $X = \text{Se}, \text{Te}$ ) are repulsive in the Franck-Condon region, meaning that the first ion signal only gives an upper limit to the energy of the first dissociative ionisation pathway ( $\text{XF}_5^+ + \text{F} + \text{e}^-$ ). Using TPEPICO time-of-flight spectra to determine the kinetic energy (KE) released in fragmentation over a range of energies, however, we have extrapolated to zero KE to calculate values of  $14.1 \pm 0.5$  and  $14.5 \pm 0.6$  eV for the first dissociative ionisation energy for  $\text{SeF}_6$  and  $\text{TeF}_6$ , respectively. Upper limits for the enthalpies of formation of  $\text{SeF}_4^+$ ,  $\text{SeF}_3^+$ ,  $\text{TeF}_4^+$  and  $\text{TeF}_3^+$  at 0K are determined to be  $426 \pm 36$ ,  $368 \pm 28$ ,  $428 \pm 36$  and  $380 \pm 28$  kJ mol<sup>-1</sup>, respectively.

## 1. Introduction

Very little is known about the positive ion thermodynamics of  $\text{SeF}_6$  and  $\text{TeF}_6$ . Potts et al. [1] and Addison et al. [2] have recorded valence photoelectron spectra (PES) from which the ionisation potentials of the various electronic states of the parent ion can be determined. However, nothing is known about how these states decay or the enthalpies of formation of any of the fragment ions that might form. Using synchrotron radiation, we have undertaken a threshold photoelectron-photoion coincidence (TPEPICO) study of these two compounds to determine some of these properties. Such determinations are also of fundamental interest, as useful insight can be gained by comparison of similar species, such as  $\text{SF}_6^+$ , as to what influences the decay dynamics of such molecular ions.

TPEPICO data on these molecules are also useful for the analysis of positive ion charge transfer data, not only in terms of thermodynamic information, but also for comparison of branching ratios at energies consistent with the recombination energy of the reactant ion. This comparison will be presented in more detail in a forthcoming publication [3].

## 2. Experimental

The experimental procedure for the acquisition of the TPEPICO data has been presented in detail previously [4, 5]. In brief, the apparatus utilises monochromatised synchrotron radiation from a 1m SEYA Namioka monochromator at the Daresbury Laboratory. This radiation ionises molecules injected effusively into an interaction region. Ions and electrons produced are extracted in opposite directions by an electric field of  $20 \text{ V cm}^{-1}$ . Threshold electrons pass through a steradiancy-type analyser and a  $127^\circ$  post analyser before being detected by a channel electron multiplier. Ions are accelerated through a linear time-of-flight (TOF) mass spectrometer incorporating space focussing. The arrival time of the ions are then recorded relative to the threshold electrons to produce fragmentation patterns of the energy-selected molecular ions. All spectra are recorded with an optical resolution of 0.3 nm. The resolution of the TOF spectra recorded in these scanning-energy experiments was set at 128 ns, which was sufficient to detect and resolve all the observed fragment ions simultaneously. The threshold electron signal, ion yield and coincidence spectra are recorded simultaneously as a function of photon energy. All spectra are normalised to the photon flux, which is recorded by a photo-multiplier tube via a sodium salicylate window.

As well as energy-selected fragmentation patterns, the kinetic energy released for a specific mode of fragmentation can also be determined from an analysis of the observed time-of-flight (TOF) peak shape of the daughter ion [6]. This experiment is performed with an improved TOF resolution than for the energy-scanning experiments from which the fragmentation patterns are determined. This experiment

was only performed here for the  $\text{XF}_5^+$  ion ( $\text{X} = \text{Se}$  or  $\text{Te}$ ). In these experiments a TOF resolution of 16 ns was used.

The  $\text{SeF}_6$  and  $\text{TeF}_6$  gases (purity *ca.* 99%) were obtained from Fluorochem Ltd. and used directly without further purification.

### 3. Results and Discussion

#### 3.1 TPES and Breakdown Diagrams

Figures 1 and 2 show the threshold photoelectron spectra (TPES) and TPEPICO branching ratios for  $\text{SeF}_6$  and  $\text{TeF}_6$ , respectively. In both cases, panel (a) shows the flux-normalised TPES, panel (b) shows the flux-normalised accumulated coincidence counts for each of the fragment ions, and panels (c) and (d) show the corresponding branching ratios as a function of energy for  $\text{XF}_5^+$ ,  $\text{XF}_3^+$ , and  $\text{XF}_4^+$ ,  $\text{XF}_2^+$ , respectively.

The first onset of signal observed in the TPES occurs at  $15.3 \pm 0.2$  eV and  $15.4 \pm 0.2$  eV for  $\text{SeF}_6$  and  $\text{TeF}_6$  respectively. These values are in approximate agreement with those obtained by Potts et al. [1] ( $\text{SeF}_6$ :  $15.4 \pm 0.2$ ;  $\text{TeF}_6$ :  $15.6 \pm 0.2$ ). The adiabatic ionisation potential (IP) of a molecule is defined as the difference in energy between the lowest lying level of the neutral ( $J''=0$ ,  $v''=0$ ) and the lowest lying level of the ion ( $J^+ = 0$ ,  $v^+ = 0$ ). Therefore, to calculate the adiabatic IP, the thermal energy of the neutral molecule prior to ionisation must be taken into account. Using vibrational frequencies taken from Claassen et al. [7] for  $\text{SeF}_6$  and  $\text{TeF}_6$ , the average internal energy is calculated to be 0.14 eV and 0.17 eV at 298K, respectively. This consequently gives the IP for  $\text{SeF}_6$  and  $\text{TeF}_6$  as  $15.4_4 \pm 0.2_0$  and  $15.5_7 \pm 0.2_0$  eV. It should also be noted that the first onset is prone to error caused by the sensitivity of the instrument, especially if there is a large change in geometry upon ionisation; that is, a more sensitive instrument should detect a signal closer to the true onset than a less sensitive one. However, we assume that this error is small compared to the errors quoted. By comparison with the known IP of  $\text{SF}_6$  ( $15.33 \pm 0.03$  eV [8]) these data show that there is an increase in the IP as one moves down the group 6B hexafluorides (i.e.  $\text{SF}_6 < \text{SeF}_6 < \text{TeF}_6$ ). This observation is in agreement with the spectra of Potts et al.[1].

By comparison with the observed TPES of  $\text{SF}_6$  recorded at a comparable resolution [9], assignments of the PE bands of  $\text{SeF}_6$  and  $\text{TeF}_6$  have been made and the states are labelled accordingly in Figures 1 and 2. In both cases, the symmetries of the X, A, B, C, D, E and F states are assumed to be as for  $\text{SF}_6$ ; that is,  $^2\text{T}_{1g}$ ,  $^2\text{T}_{1u}$ ,  $^2\text{T}_{2u}$ ,  $^2\text{E}_g$ ,  $^2\text{T}_{2g}$ ,  $^2\text{T}_{1u}$  and  $^2\text{A}_{1g}$ , respectively. For  $\text{SeF}_6$  the relative intensities and energies of the photoelectron bands are similar to those observed for  $\text{SF}_6$ , allowing us to feel confident

with this assignment. We should note that the A and B bands are not resolved at this resolution in either molecule [9]. The main difference appears to be a general reduction in the energy separation of the electronic states. For TeF<sub>6</sub>, if our assignment is correct, this reduction is even more pronounced with the A, B and C states all merging into one photoelectron band. Support for this effect comes from a comparison of the X-F bond-length of the three molecules (SF<sub>6</sub>: 1.557 ± 0.001 Å [10]; SeF<sub>6</sub>: 1.678 ± 0.001 Å [11]; TeF<sub>6</sub>: 1.824 ± 0.004 Å [12]). The implication of this increase in bond-length along the series S, Se, Te is that interactions between the fluorine atoms, which one might expect to cause a spreading of the energies of the observed ionic electronic states, will decrease as one moves down the group, consequently reducing the energy differences between the states.

The breakdown diagrams for SeF<sub>6</sub>, TeF<sub>6</sub> (and also SF<sub>6</sub> [9]) are qualitatively very similar. In all three, the parent molecular ion is absent and XF<sub>5</sub><sup>+</sup> appears at the onset of ionisation. The ground electronic states of all three ions must therefore be repulsive in the Franck-Condon region. As the ionisation energy is increased, XF<sub>4</sub><sup>+</sup> is formed, closely followed within about 1 eV by XF<sub>3</sub><sup>+</sup>, with XF<sub>2</sub><sup>+</sup> being formed at higher energies still. SeF<sub>6</sub> appears to behave almost exactly like SF<sub>6</sub>, with the higher-energy part of the C state of the parent ion dissociating into SeF<sub>4</sub><sup>+</sup>, the D state dissociating into SeF<sub>4</sub><sup>+</sup> and SeF<sub>3</sub><sup>+</sup>, and the E state dissociating into SeF<sub>3</sub><sup>+</sup>. TeF<sub>6</sub>, by contrast, does not produce TeF<sub>4</sub><sup>+</sup> or TeF<sub>3</sub><sup>+</sup> until the E state.

The experimental appearance energies of the fragment ions XF<sub>5</sub><sup>+</sup>, XF<sub>4</sub><sup>+</sup>, XF<sub>3</sub><sup>+</sup> and XF<sub>2</sub><sup>+</sup> for SeF<sub>6</sub> and TeF<sub>6</sub> are shown in Table 1. Also shown are experimental data for SF<sub>6</sub> taken from Creasey et al. [9]. The lowest possible observable appearance energy for a particular fragment ion can be estimated from:

$$AE(\text{lowest}) \cong \Delta_f H[\text{products}]_{0\text{K}} - \Delta_f H[\text{XF}_6]_{298\text{K}}$$

This corresponds to reactant molecules with the mean internal energy at 298K forming products in their lowest rovibronic energy levels and with no relative translation. This neglects the possible lowering of the appearance energy due to the presence of XF<sub>6</sub> molecules containing more than the average amount of internal energy at 298K. Estimates of this lowering indicate that it is unlikely to exceed 20 kJ mol<sup>-1</sup>. The observed appearance energy will be an upper bound to AE(lowest), as it may not be possible to access the products in their lowest rovibronic state. Therefore, by taking the enthalpies of formation of the neutrals at 298K (-1117 ± 21 kJ mol<sup>-1</sup> for SeF<sub>6</sub>, -1318 ± 21 kJ mol<sup>-1</sup> for TeF<sub>6</sub> [8]) and the enthalpies of formation of F and F<sub>2</sub> (77.3 ± 0.3 and 0 kJ mol<sup>-1</sup>, respectively [8]), an upper limit for the 0K enthalpies of formation of the fragment ions can be calculated. Calculations for the smaller fragments obviously depend on whether F<sub>2</sub> is formed as the parent molecular ion dissociates. In Table 1 we have listed the limits for

these enthalpies of formation, calculated assuming both that  $F_2$  forms and that only  $nF$  forms ( $n = 1$  to  $4$ ). For the  $XF_2^+$  calculation, we have assumed that  $2F_2$  molecules are the neutrals in the ‘ $F_2$  formed’ calculation. For comparison, these calculations were also performed for the experimental data of Creasey et al. on  $SF_6$  [9]. Finally, we have included in Table 1 the known enthalpies of formation (at 298K) of the fragment ions of  $SF_6$ . Data for  $SF_4^+$ ,  $SF_3^+$  and  $SF_2^+$  were taken from Lias et al [8]. The value for  $SF_5^+$  was taken from a study of the kinetics of the  $HCl^+ + SF_6 \rightarrow SF_5^+ + HF + Cl$  ion-molecule reaction [13]. This value is  $45 \text{ kJ mol}^{-1}$  lower than that obtained by Lias et al [8]. We comment that the Lias et al. value was obtained from a study of the kinetics of the  $CF_3^+ + SF_6 \rightarrow SF_5^+ + CF_4$  ion-molecule reaction, where the enthalpy of formation of  $CF_3^+$  is of critical importance. This value for  $CF_3^+$  has been the subject of recent controversy [14, 15], and for this reason we prefer the value for  $SF_5^+$  of Tichy et al. [13].

As stated above, all three species behave similarly in regards to their fragmentation. Therefore it seems reasonable to draw some conclusions about the calculated thermochemical onsets from a comparison with the  $SF_6$  data. For  $SF_6$  it can be seen that the onsets for  $SF_4^+$  and  $SF_3^+$  lie very close to the thermochemical threshold, if the neutral products are  $2F$  and  $3F$  respectively. Therefore it seems plausible that  $SeF_6$  and  $TeF_6$  behave in a similar way. In other words, the enthalpies of formation of  $SeF_4^+$ ,  $SeF_3^+$ ,  $TeF_4^+$  and  $TeF_3^+$  are likely to be close to  $426 \pm 36$ ,  $368 \pm 28$ ,  $428 \pm 36$  and  $380 \pm 28 \text{ kJ mol}^{-1}$ , respectively.

Since  $SF_5^+$  and  $SF_2^+$  have their first appearance energies well in excess of the thermochemical threshold for  $SF_{6-n}^+ + nF$  production, then we cannot narrow down any further our choice of limits for the Se and Te containing ions from these data alone. The reason why  $SF_5^+$  does not form at its thermochemical threshold is simply because the IP of  $SF_6$  lies well above the  $SF_5^+ + F$  dissociative ionisation limit. The reason why  $SF_2^+$  does not form at its thermochemical threshold is not clear from these data alone.

### 3.2 Kinetic energy release measurements

As neither  $SeF_6^+$  or  $TeF_6^+$  are observed in the scanning-energy TPEPICO experiment, the ground electronic states of both molecular ions are anticipated to be repulsive in the Franck-Condon region. This then implies that the thermochemical limit to form  $XF_5^+$  will lie below the observed onset of ionisation. Throughout this Letter we use the phrase ‘dissociative ionisation energy’ to describe the energy of  $XF_5^+ + F + e^-$  relative to the ground state of  $XF_6$ . In the case of  $SF_6$ , although the IP occurs at  $15.33 \pm 0.03 \text{ eV}$  [8], the dissociative ionisation energy to form  $SF_5^+$  is  $14.0 \pm 0.1 \text{ eV}$  [13]. Therefore, to obtain a more accurate value for the enthalpy of formation of  $SeF_5^+$  and  $TeF_5^+$  we have attempted to measure the kinetic

energy released in fragmentation close to threshold. If a molecular ion decays statistically, the onset of the first fragment ion should also correspond to the dissociative ionisation energy. Consequently, there is essentially zero energy released into fragmentation at this excitation energy. In the case of  $\text{SeF}_6$ ,  $\text{TeF}_6$  (and  $\text{SF}_6$ ), however, the first onset is likely to be above the dissociative ionisation energy for the reasons stated above, so the kinetic energy released in fragmentation will be non-zero. Therefore, the kinetic energy released in fragmentation will give a lower limit of how much 'extra' energy is available to the dissociation process. However, as the percentage of the available energy that is released into translation is not known due to a lack of knowledge of the decay dynamics, a single kinetic energy release measurement will not provide an absolute value for the dissociative ionisation energy. For example, in a statistical dissociation, the excess energy is randomised into all the molecular vibrations and a comparatively low kinetic energy release would be observed [16]. Conversely, if the parent ion decays impulsively, as is likely to be the case here, there is not enough time for randomisation of the energy to occur and substantially more energy will be partitioned into translation [17]. Furthermore, the amount of kinetic energy observed in an impulsive decay will depend on how rigid the fragment ion remains as it dissociates [18]. We have therefore attempted to measure the kinetic energy released in fragmentation over a range of energies from *ca.* 15.7 to 17.7 eV to see if any patterns in the decay mechanism can be discerned. If the pattern is clear it should then be possible to predict at what photon energy the kinetic energy released in fragmentation is zero. This energy should correspond to the dissociative ionisation energy.

Figures 3 and 4 show the results obtained for  $\text{SeF}_6$  and  $\text{TeF}_6$ , respectively. Panel (a) reveals the measured kinetic energy released into fragmentation and panel (b) shows the TPES for comparison over the appropriate energy region. The kinetic energy was extracted from the TOF spectra in a more simplified way to that usually used [6]. Each TOF spectrum was assumed to represent a single kinetic energy release (rather than a distribution of releases) convoluted with the thermal energy of the molecules prior to ionisation. All isotopes of Se and Te were considered (their masses and natural abundance taken from [19]), and the size of the kinetic energy release was varied until a minimum in the sum of the squares of the errors was obtained. As examples, Figure 5 shows two typical TOF spectra for  $\text{SeF}_6$  (upper panel) and  $\text{TeF}_6$  (lower panel) recorded at photon energies of 16.8 and 16.9 eV, from which kinetic energy releases of 0.83 and 0.69 eV, respectively, were obtained. The simplification of assuming only a single release was introduced to reduce the fitting time and parameters involved. A few TOF spectra were checked more rigorously using a range of kinetic energy releases [6], but results showed little deviation from those seen in Figures 3 and 4.

Although there is considerable scatter in the data for both  $\text{SeF}_5^+$  and  $\text{TeF}_5^+$ , there is a clear general trend of a linear increase in the observed kinetic energy release with photon energy for both ions. This is to be expected as most kinetic energy release models for impulsive decay predict a linear relationship



between the available energy and the kinetic energy released [17, 18]. The solid lines in Figures 3 and 4 are the linear least-squares fits to the data which were used to perform the extrapolation to zero kinetic energy. A further conclusion from the data is that the decay mechanism does not change in a dramatic way across the energy range studied. If it did, then a clear deviation from the straight line relationship for the kinetic energy released might be observed. Providing the mechanism of decay for the molecular ion does not change if it were accessed at energies below 15.7 eV, then the extrapolation of the linear fit to zero kinetic energy will give the dissociative ionisation energy to form  $\text{XF}_5^+ + \text{F} + \text{e}^-$ . This was determined to be  $14.1 \pm 0.5$  eV and  $14.5 \pm 0.5$  eV for  $\text{SeF}_6$  and  $\text{TeF}_6$ , respectively. From these dissociation energies it is possible to calculate the enthalpies of formation of the fragment ions  $\text{SeF}_5^+$  and  $\text{TeF}_5^+$  to be  $166 \pm 52$  and  $4 \pm 62$   $\text{kJ mol}^{-1}$ , respectively.

Interestingly, the slope of the straight line fit of the kinetic energy release as a function of the photon energy is similar for both  $\text{SeF}_6$  and  $\text{TeF}_6$ , showing that  $\sim 30\%$  of the available energy is released into translation. This indicates that a similar decay mechanism is taking place for both molecules. This fractional release is substantially less than that predicted by a pure impulsive model [17]; the predicted releases for  $\text{SeF}_5^+$  and  $\text{TeF}_5^+$  are 89% and 94%, respectively. Clearly this model does not accurately describe the decay process. To calculate the energy released by a statistical model, knowledge of the vibrational frequencies of the daughter ion is required. These are not available, though it is possible to estimate a lower limit to the release by [20] :

$$\text{Kinetic energy released} \geq \text{Available Energy} / (x+1),$$

where  $x$  is the number of vibrational degrees of freedom in the transition state. For both molecules, with  $x = 15$  this leads to a fractional release of  $\sim 6\%$ . The observed releases therefore lie between the statistical and pure impulsive models. This may indicate that the excited  $\text{XF}_6^+$  ions ( $\text{XF}_6^{+*}$ ) survive long enough for some randomisation of the available energy to take place before dissociation occurs. One might expect that such a mechanism would produce a non-linear relationship of the kinetic energy release with the photon energy if the process depends critically on the lifetime of  $\text{XF}_6^{+*}$ . However, since our data appear to give a linear relationship within experimental error and the dissociative ionisation energies are similar to those obtained for  $\text{SF}_6$  [13], we feel confident in our estimates of these first dissociative ionisation energies of  $\text{SeF}_6$  and  $\text{TeF}_6$ . The sizeable errors are likely to account for any non-linearity in the decay pattern that may be present below the IP of each molecule.

## 4. Conclusions

By performing TPEPICO spectroscopy on SeF<sub>6</sub> and TeF<sub>6</sub>, upper limits on the enthalpies of formation of their fragment ions have been determined from their experimental onsets. By using the kinetic energy released in fragmentation over a range of photon energies, the first dissociative ionisation limit to XF<sub>5</sub><sup>+</sup> + F + e<sup>-</sup> has been determined using an extrapolation procedure. Although errors in such a measurement are large due to considerable scatter in the data, this experiment proves that such a determination can be informative. With improved statistics from longer acquisition times, it might be possible to reduce these errors considerably. Due to beam-time constraints, however, such measurements are impractical at present and the efficiency of the experiment specifically for the measurement of TOF spectra would need improvement. For example, the use of a cooled molecular beam sample would help by reducing the thermal population observed in the TOF spectra. With decreased errors, the appearance of fine structure in the kinetic energy release as a function of the available energy may provide more details on the mechanisms of decay.

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**Table 1.** Thermochemistry of fragment ions produced from photoionisation of SF<sub>6</sub>, SeF<sub>6</sub> and TeF<sub>6</sub>

Parent	Fragment	AE (eV) <sup>a</sup>	$\Delta_f H^{a,b}$ (kJ mol <sup>-1</sup> ) (F <sub>2</sub> formed)	$\Delta_f H^{a,b}$ (kJ mol <sup>-1</sup> ) (nF formed)	$\Delta_f H^{c,d,e}$ (kJ mol <sup>-1</sup> )
<b>SF<sub>6</sub></b>	SF <sub>5</sub> <sup>+</sup>	15.5 ± 0.2	-	197 ± 20	52
	SF <sub>4</sub> <sup>+</sup>	18.4 ± 0.3	554 ± 29	399 ± 29	403
	SF <sub>3</sub> <sup>+</sup>	19.2 ± 0.3	554 ± 29	399 ± 29	376
	SF <sub>2</sub> <sup>+</sup>	27.0 ± 0.5	1384 ± 48	1074 ± 48	678
<b>SeF<sub>6</sub></b>	SeF <sub>5</sub> <sup>+</sup>	15.3 ± 0.2	-	281 ± 28	166 ± 52
	SeF <sub>4</sub> <sup>+</sup>	17.6 ± 0.2	581 ± 36	426 ± 36	~426 ± 36
	SeF <sub>3</sub> <sup>+</sup>	17.8 ± 0.2	523 ± 28	368 ± 28	~368 ± 28
	SeF <sub>2</sub> <sup>+</sup>	23.6 ± 0.2	1160 ± 28	850 ± 28	<850 ± 28
<b>TeF<sub>6</sub></b>	TeF <sub>5</sub> <sup>+</sup>	15.4 ± 0.2	-	90 ± 28	4 ± 62
	TeF <sub>4</sub> <sup>+</sup>	19.7 ± 0.3	583 ± 36	428 ± 36	~428 ± 36
	TeF <sub>3</sub> <sup>+</sup>	20.0 ± 0.2	535 ± 28	380 ± 28	~380 ± 28
	TeF <sub>2</sub> <sup>+</sup>	23.0 ± 0.2	901 ± 28	591 ± 28	<591 ± 28

<sup>a</sup> Values for SF<sub>6</sub> from Creasey et al. [9]

<sup>b</sup> Upper limits for the enthalpies of formation of the fragment ions calculated from the appearance energies as observed in the TPEPICO experiment. The first column indicates the limit if F<sub>2</sub> is allowed as one (or both in the case of XF<sub>2</sub><sup>+</sup>) of the neutrals, the second if only nF is allowed.

<sup>c</sup> Literature values for the enthalpies of formation of the fragment ions from SF<sub>6</sub> extracted from refs [8] and [13] – see text.

<sup>d</sup> Values given in this column for SeF<sub>6</sub> and TeF<sub>6</sub> represent our best estimates of the enthalpies of formation of the fragment ions as discussed in the text. For XF<sub>5</sub><sup>+</sup>, the values given are calculated from our analysis of the kinetic energy released in fragmentation.

<sup>e</sup> Note that literature values are at 298K whereas those calculated from the TPEPICO work will be more consistent with 0 K enthalpies of formation. However, differences are likely to be < 20 kJ mol<sup>-1</sup>.

## Figure Captions

**Figure 1.** (a) Threshold photoelectron spectrum of  $\text{SeF}_6$  at a resolution of 0.3 nm (b) TPEPICO coincidence ion yields of  $\text{SeF}_5^+$ ,  $\text{SeF}_4^+$ ,  $\text{SeF}_3^+$  and  $\text{SeF}_2^+$ . (c) Branching ratios for  $\text{SeF}_5^+$  and  $\text{SeF}_3^+$  production. (d) Branching ratios for  $\text{SeF}_4^+$  and  $\text{SeF}_2^+$  production.

**Figure 2.** (a) Threshold photoelectron spectrum of  $\text{TeF}_6$  at a resolution of 0.3 nm (b) TPEPICO coincidence ion yields of  $\text{TeF}_5^+$ ,  $\text{TeF}_4^+$ ,  $\text{TeF}_3^+$  and  $\text{TeF}_2^+$ . (c) Branching ratios for  $\text{TeF}_5^+$  and  $\text{TeF}_3^+$  production. (d) Branching ratios for  $\text{TeF}_4^+$  and  $\text{TeF}_2^+$  production.

**Figure 3.** (a) Measured total kinetic energy released in the process  $\text{SeF}_6 + h\nu \rightarrow \text{SeF}_5^+ + \text{F} + \text{e}^-$  for photon energies in the range 15.7 to 17.7 eV. A linear extrapolation to zero kinetic energy gives the dissociative ionisation energy of the reaction. The error in each value of the total kinetic energy is *ca.* 20%. (b) Threshold photoelectron spectrum of  $\text{SeF}_6$ .

**Figure 4.** (a) Measured total kinetic energy released in the process  $\text{TeF}_6 + h\nu \rightarrow \text{TeF}_5^+ + \text{F} + \text{e}^-$  for photon energies in the range 15.7 to 17.7 eV. A linear extrapolation to zero kinetic energy gives the dissociative ionisation energy of the reaction. The error in each value of the total kinetic energy is *ca.* 20%. (b) Threshold photoelectron spectrum of  $\text{TeF}_6$ .

**Figure 5.** TPEPICO-TOF spectra (symbols) for (a)  $\text{SeF}_5^+/\text{SeF}_6$  and (b)  $\text{TeF}_5^+/\text{TeF}_6$  recorded at a photon energy of 16.8 eV and 16.9 eV respectively. Shown as lines, the data fit to single kinetic energy releases of 0.83 and 0.69 eV, respectively (see text).

Figure 1

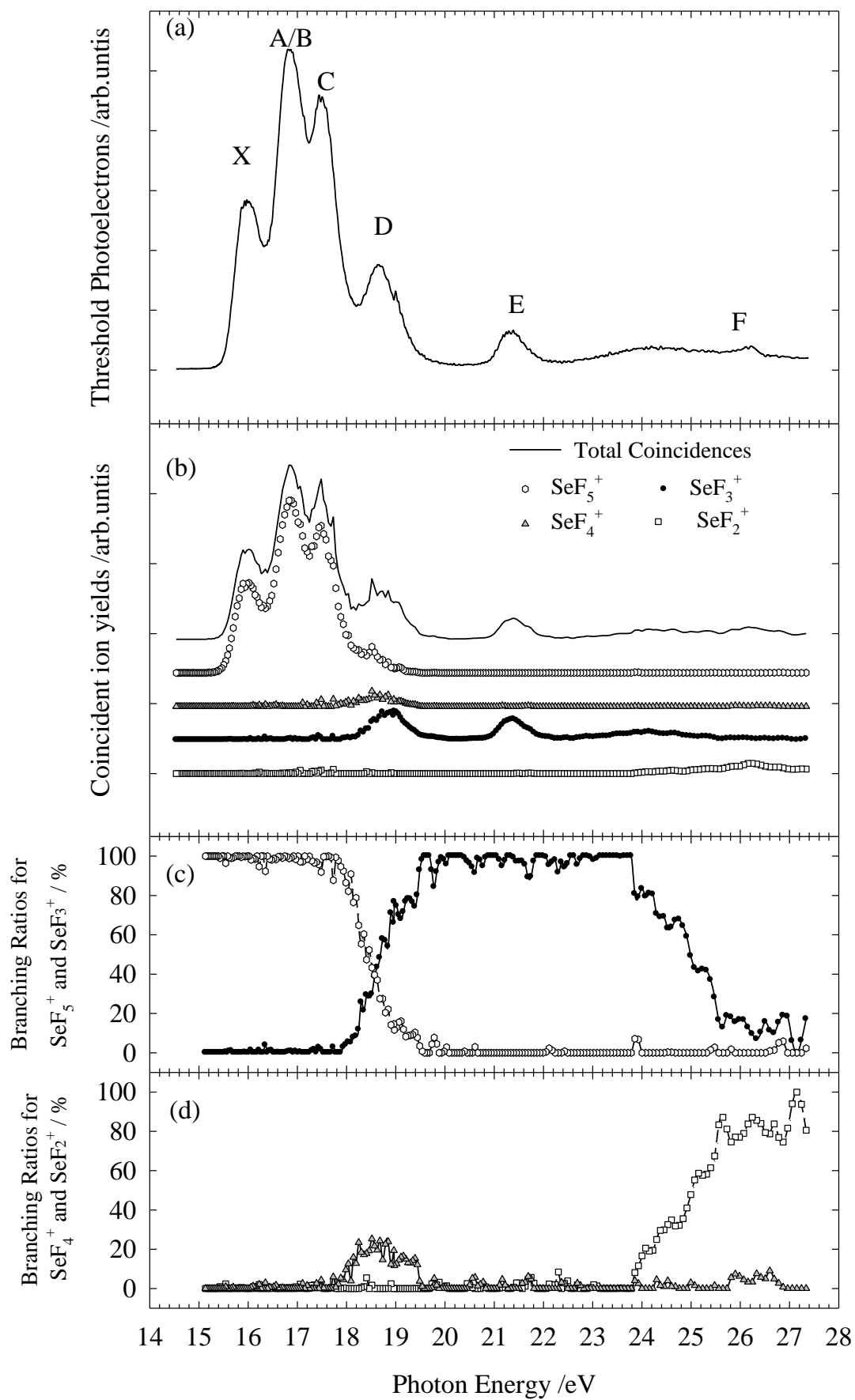


Figure 2

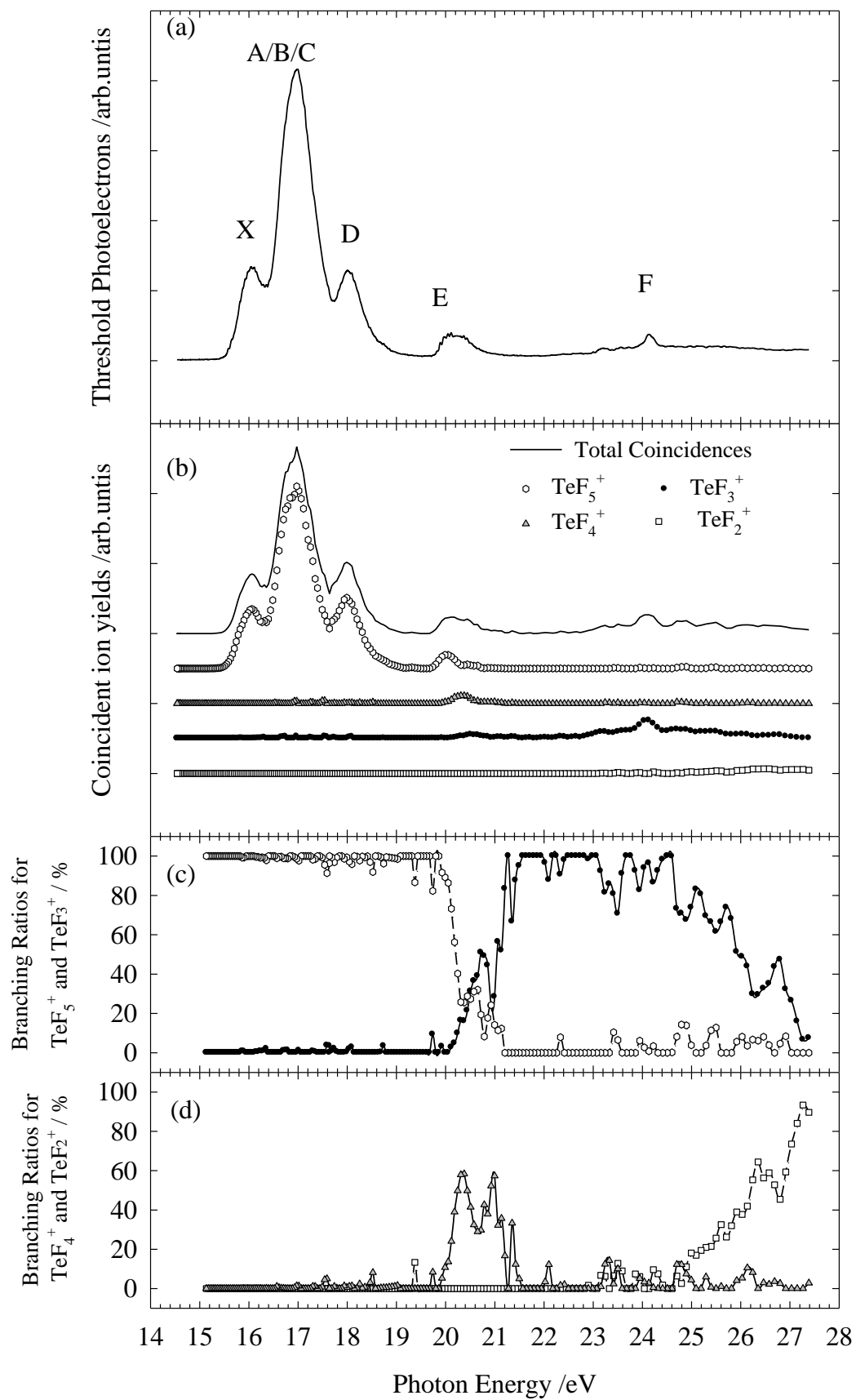


Figure 3

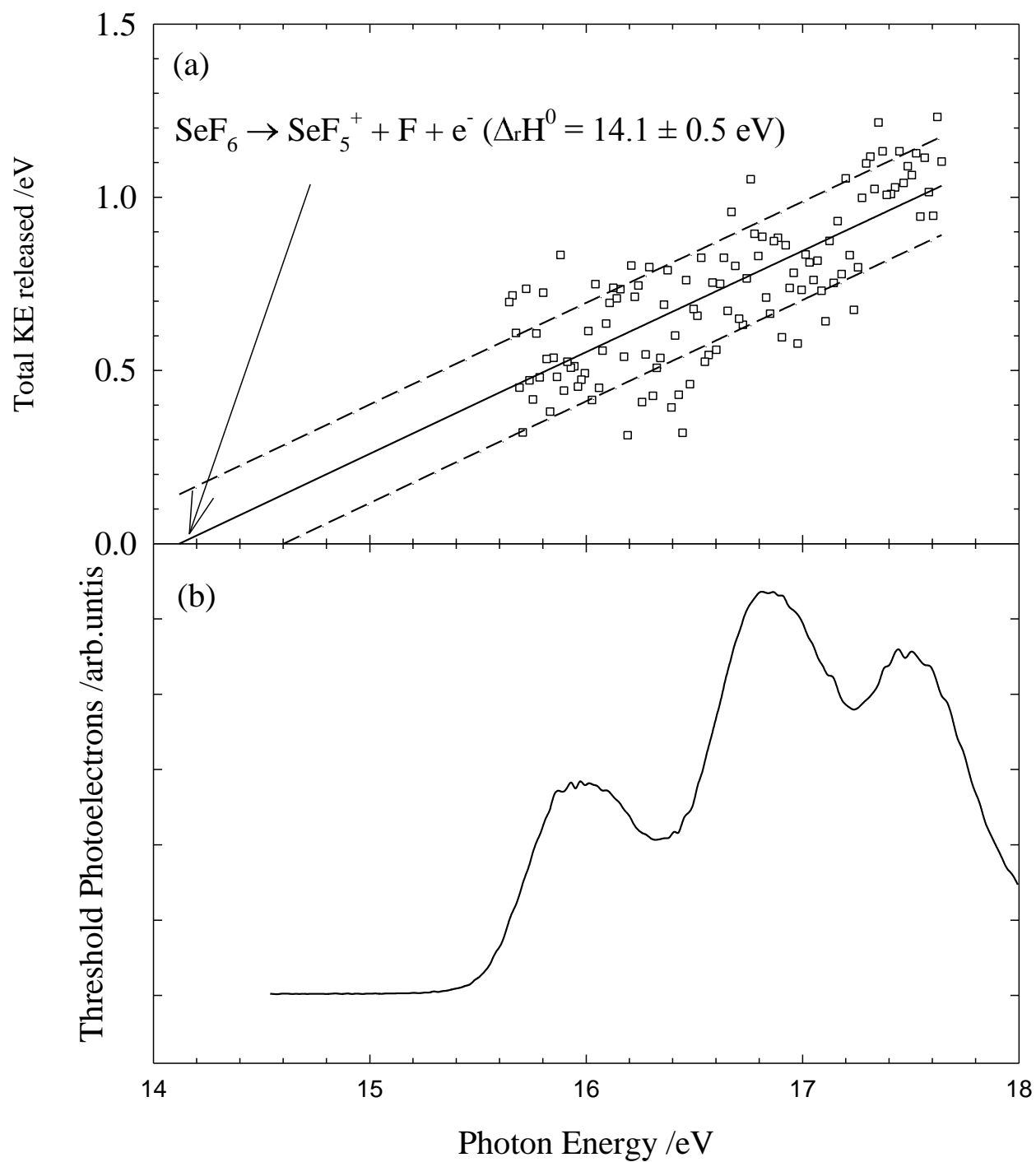




Figure 4

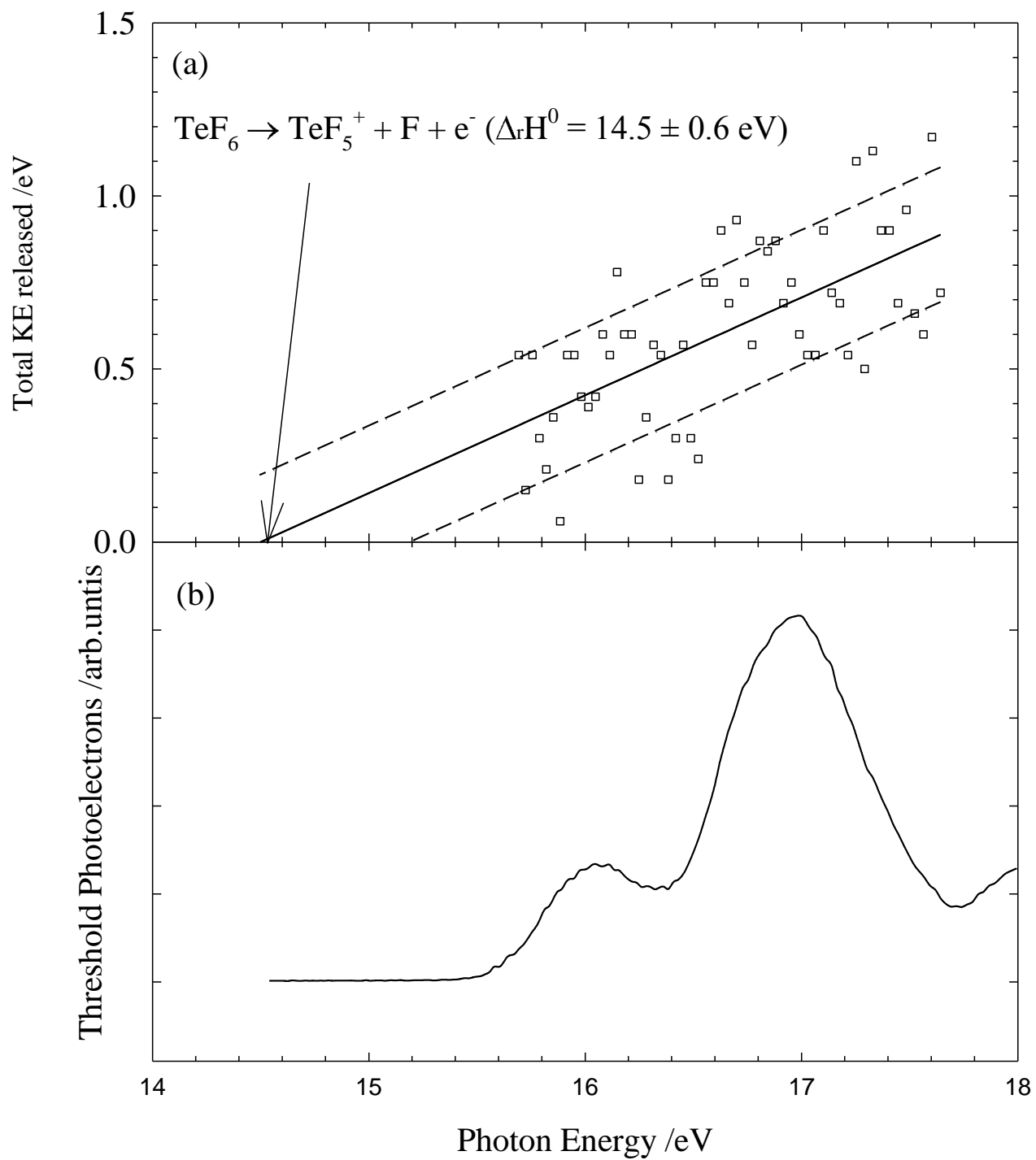


Figure 5

