

## Vacuum-Ultraviolet Negative Photoion Spectroscopy of SF<sub>5</sub>Cl

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Professor Richard Tuckett (University of Birmingham) / July 2011

# Vacuum-UV negative photoion spectroscopy of SF<sub>5</sub>Cl

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Using vacuum-UV radiation from a synchrotron, gas-phase negative ions are detected by mass spectrometry following photoexcitation of SF<sub>5</sub>Cl. F<sup>-</sup>, Cl<sup>-</sup> and SF<sub>5</sub><sup>-</sup> are observed, and their ion yields recorded in the range 8–30 eV. F<sup>-</sup> and Cl<sup>-</sup> show a linear dependence of signal with pressure, showing that they arise from unimolecular ion-pair dissociation, generically written  $AB + h\nu \rightarrow C^- + D^+ (+ \text{neutral(s)})$ . F<sup>-</sup> is the strongest signal, and absolute cross sections are determined by calibrating the signal intensity with that of F<sup>-</sup> from SF<sub>6</sub> and CF<sub>4</sub>. Resonances are observed, and assigned to transitions to Rydberg states of SF<sub>5</sub>Cl. The Cl<sup>-</sup> signal is much weaker, despite the S–Cl bond being significantly weaker than the S–F bond. Appearance energies for F<sup>-</sup> and Cl<sup>-</sup> of  $12.7 \pm 0.2$  and  $10.6 \pm 0.2$  eV are determined. The spectra suggest that these ions form indirectly by crossing of Rydberg states of SF<sub>5</sub>Cl onto an ion-pair continuum.

**KEYWORDS** : sulfur chloropentafluoride ; ion-pair formation ; vacuum-UV ; absolute cross sections

## 1. Introduction

There have been many investigations of the ion chemistry of sulfur hexafluoride, SF<sub>6</sub>, involving production of cations, anions, and chemical reactions,<sup>1-3</sup> but relatively few of the derivative molecule sulfur chloropentafluoride, SF<sub>5</sub>Cl. The structure of SF<sub>5</sub>Cl, C<sub>4v</sub> symmetry in the gas phase, has been established by microwave spectroscopy<sup>4</sup> and electron diffraction.<sup>5</sup> Four equatorial S–F bonds have a slightly longer length, 0.157 nm, than the S–F axial bond, 0.159 nm, whilst that of S–Cl is significantly longer, 0.204 nm. There have only been two photoelectron studies of this molecule, one using fixed-energy He I and He II resonance lines<sup>6</sup> and one using tunable vacuum-UV (VUV) photons coupled with threshold electron detection.<sup>7</sup> The relative ordering of the valence molecular orbitals (MO) has been calculated using self-consistent discrete variational X $\alpha$  methods.<sup>8</sup> The state-selected fragmentation dynamics of the electronic states of SF<sub>5</sub>Cl<sup>+</sup> has been studied by threshold photoelectron photoion coincidence spectroscopy.<sup>7</sup> This publication also reported results from a Gaussian 03 calculation<sup>9</sup> which supported the MO assignments made by Klyagina *et al.*<sup>8</sup> Figure 1 summarises the combined findings of these investigations, and correlates the MOs for SF<sub>5</sub>Cl with those of SF<sub>6</sub> of O<sub>h</sub> symmetry. While the ordering of the valence MOs in for SF<sub>6</sub> is well established,<sup>10</sup> we note that the ordering and assignments given for SF<sub>5</sub>Cl are based on more limited evidence. The kinetics and ionic products of the reactions of a large number of small cations with SF<sub>5</sub>Cl have been studied in a selected ion flow tube.<sup>11</sup>

The studies of anion production following excitation of SF<sub>5</sub>Cl are even more limited. There have been two measurements of the thermal electron attachment rate coefficient to SF<sub>5</sub>Cl :  $(4.8 \pm 1.2) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  by van Doren *et al.*<sup>12</sup> and  $(2.0 \pm 0.3) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$  by Mayhew *et al.*,<sup>13</sup> a factor of *ca.* 5–12 slower than the value for SF<sub>6</sub>,  $(2.38 \pm 0.15) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ .<sup>14</sup> Under thermal electron conditions, electron attachment to SF<sub>5</sub>Cl is dissociative, producing SF<sub>5</sub><sup>-</sup> (92%), Cl<sup>-</sup> (5%) and FCl<sup>-</sup> (3%), whereas that to SF<sub>6</sub> is predominantly non-dissociative. A recent crossed beam study of SF<sub>5</sub>Cl with low-energy electrons in the range 0–14 eV<sup>15</sup> has clarified inconsistencies arising from two earlier studies.<sup>16,17</sup> As in the thermal experiment, electron attachment is dissociative with SF<sub>5</sub><sup>-</sup> being the dominant anion at low electron energies, but resonances

forming  $F^-$ ,  $Cl^-$  and  $FCl^-$  are now observed at  $E > 3$  eV. The experimental study by van Doren *et al.* stimulated an extensive *ab initio* study of the structures and enthalpies of formation of  $SF_nCl$  ( $n = 0-5$ ) and their anions.<sup>18</sup>

In this paper, we report the first study of ion-pair formation in  $SF_5Cl$  following tunable VUV photoexcitation in the range 10–30 eV from a synchrotron. It continues our earlier study on  $SF_5$ -containing molecules,  $SF_6$  and  $SF_5CF_3$ .<sup>19</sup> Cross sections for anion production are put onto an absolute scale by calibration of the signals with that of  $F^-$  from  $SF_6$  and  $CF_4$ ,<sup>2,20</sup> but quantum yields for their production cannot be determined because there are no reported values of the total absorption cross section in this region of the VUV.

## 2. Experimental

The ion-pair apparatus, described in detail elsewhere,<sup>21</sup> comprises a crossed effusive beam of the molecular sample with tunable VUV radiation from beamline 3.1 (1-metre Wadsworth) of the Daresbury, UK synchrotron source.<sup>22</sup> There is no internal cooling of the sample in the effusive beam. Anions are detected on the third orthogonal axis by a Hiden Analytical HAL IV triple quadrupole mass spectrometer (QMS) which is differentially pumped from the interaction region to reduce the number of free electrons and secondary collisions. Two gratings cover the wide range of the vacuum-UV: the high-energy grating covering *ca.* 12–35 eV, and the low-energy grating covering *ca.* 8–18 eV. The optimum resolution of the beamline is 0.05 nm, corresponding to *ca.* 0.01 eV at 15 eV. However, to enhance sensitivity, the spectra reported here were recorded with degraded resolution. A 2 mm diameter, 300 mm long capillary light guide connects the beamline to the experimental apparatus, providing the necessary differential pumping.

Ion yields were determined by recording the yield of an anion of defined  $m/z$  as the beamline monochromator was scanned. The signals are first normalised to photon flux, ring current, gas pressure, ionization gauge sensitivity, and relative mass sensitivity of the QMS to detection of the different anions;

full details are given elsewhere.<sup>23</sup> These signals are then put onto an absolute scale by determining the  $F^-$  intensity in the experiment from  $SF_6$  and  $CF_4$ , and calibrating them to values of the cross section determined by Mitsuke *et al.* for  $SF_6$  ( $(7 \pm 2) \times 10^{-21} \text{ cm}^2$  at 14.3 eV) and  $CF_4$  ( $(1.25 \pm 0.25) \times 10^{-21} \text{ cm}^2$  at 13.9 eV).<sup>2,20</sup> We estimate that the cross sections are accurate to a factor of *ca.* 2.  $F^-$ ,  $Cl^-$  and  $SF_5^-$  were the only anions detected. The variation of anion signal with pressure was determined for all three anions over the range *ca.*  $(0.5\text{--}5.0) \times 10^{-5}$  mbar.  $F^-$  and  $Cl^-$  show a linear dependence with pressure, showing that these ions form by an ion-pair process. That is, an anion and cation are produced simultaneously in the photon-induced reaction, which we write generically as  $AB + h\nu \rightarrow C^- + D^+ (+ \text{neutral(s)})$ .  $SF_5^-$  shows a non-linear dependence with pressure, with the signal rising more rapidly with pressure than from a linear relationship. This suggests that  $SF_5^-$  likely results from the two-step process of dissociative electron attachment. That is,  $SF_5Cl + h\nu \rightarrow SF_5Cl^+ + e^-$ , followed by  $SF_5Cl + e^- \rightarrow SF_5^- + Cl$ , where a quadratic dependence of  $SF_5^-$  signal with pressure is predicted.

The  $SF_5Cl$  sample was provided by Apollo Scientific with a quoted purity of *ca.* 97%. Impurities of  $SF_4$ ,  $FCl$  and  $Cl_2$  have been noted in previous studies using  $SF_5Cl$  samples, and small amounts of  $SF_xO_y$  species have also been detected – identified as by-products in the industrial production of  $SF_5Cl$  from the hydrolysis of  $SF_4$ .<sup>7,14</sup> The effect of any contributions from these impurities to the anion spectra cannot be quantified, but is probably very small. Production of  $F^-$  from  $SF_4$  and  $FCl$  is likely to be the biggest contaminant, so the values of the cross section for  $F^-$  production from  $SF_5Cl$  (Section 4.1 and Figure 2) are upper limits.

### 3. Thermochemistry

This work determines appearance energies at 298 K ( $AE_{298}$ ) for fragment anions formed from photoexcitation of  $SF_5Cl$ , and they are compared with calculated thermochemical values. Berkowitz has noted that for many polyatomic molecules, when suitable assumptions are made about the nature of the accompanying cation and neutral fragment(s), a calculated threshold energy is a lower limit to the experimental  $AE_{298}$  of an anion.<sup>24</sup> For the generic ion-pair reaction  $AB + h\nu \rightarrow C^- + D^+ (+ \text{neutrals(s)})$ , this inequality can be written:

$$AE(C^-) \geq D_o(A-B) + IE(C) - EA(D) \quad (I)$$

where  $D_o$  is a bond dissociation energy, IE an ionisation energy and EA an electron affinity. Furthermore, in comparing  $AE_{298}$  values with calculated enthalpies of appropriate dissociation reactions at 298 K,  $\Delta_r H^\circ_{298}$ , two assumptions are being made which are justified at the relatively modest resolution of the experiment, *ca.* 0.1–0.2 eV. First, although an  $AE_{298}$  value cannot be equated to  $\Delta_r H^\circ_{298}$  because of thermal effects,<sup>25</sup> the corrections needed to the  $AE_{298}$  values are typically less than 0.1 eV and they can be ignored. Second, the effects of entropy are disregarded, even though all unimolecular reactions involve  $\Delta n > 0$ , where  $\Delta n$  is the stoichiometric number of product species minus the number of reactant species. This is justified because the  $|\Delta_r H^\circ_{298}|$  values are all large.

Values for  $\Delta_r H^\circ_{298}$  of relevant ion-pair reactions were calculated using literature values for enthalpies of formation ( $\Delta_f H^\circ_{298}$  in  $\text{kJ mol}^{-1}$ ):  $\text{SF}_5\text{Cl} = -1039$ ,  $\text{SF}_4\text{Cl} = -761$ ,  $\text{SF}_5 = -915$ ,  $\text{SF}_4 = -768$ ,  $\text{SF}_3 = -442$ ,  $\text{SF}_2 = -295$ ,  $\text{FCl} = -50$ ,  $\text{Cl} = +121$ ,  $\text{F} = +79$ ;  $\text{SF}_5^- = -1282$ ,  $\text{Cl}^- = -227$ ,  $\text{F}^- = -249$ ;  $\text{SF}_4\text{Cl}^+ \leq +327$ ,  $\text{SF}_5^+ = +29$ ,  $\text{SF}_4^+ = +389$ ,  $\text{SF}_3^+ = +361$ ,  $\text{SF}_2^+ = +693$ ,  $\text{SF}^+ = +998$ ,  $\text{Cl}^+ = +1372$ .<sup>7,11,26-29</sup> Where multiple values for a species which differ significantly from each other are given in the literature, a subjective choice has been made for the preferred value.

## 4. Results and discussion

Only three anions,  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{SF}_5^-$ , were detected following VUV photoexcitation of  $\text{SF}_5\text{Cl}$ . The  $\text{F}^-$  signal was by far the strongest, followed by  $\text{Cl}^-$ , whilst  $\text{SF}_5^-$  was only just detected above the sensitivity limit of the apparatus. The strength of the  $\text{F}^-$  signal may initially appear somewhat surprising, given that the  $\text{F}_4\text{ClS}-\text{F}$  bond dissociation energy, 3.70 eV, is stronger than that of  $\text{F}_5\text{S}-\text{Cl}$ , 2.54 eV.<sup>11,26,28</sup>

### 4.1 Formation of $\text{F}^-$

The cross section for  $F^-$  formation is shown in Figure 2(a) over the range 12–30 eV. The  $F^-$  signal increased linearly with increasing  $SF_5Cl$  gas pressure, indicating it is formed *via* unimolecular ion-pair dissociation. The onset for  $F^-$  production is  $12.7 \pm 0.2$  eV (Figure 2(b)), and we note that this value lies *above* the adiabatic ionization energy for  $SF_5Cl$ , 12.3 eV.<sup>6,7</sup> The onset is gradual and the cross section increases at a steady gradient up to *ca.* 13.6 eV (labelled ‘1’ in Figure 2(b)). Above this energy, the gradient increases and leads to a cross section maximum of  $6.1 \times 10^{-20}$  cm<sup>2</sup> at 14.06 eV (‘2’ in Figure 2(b)). The shoulder between 12.7–13.6 eV may arise from one or more of the following ion-pair dissociation reactions:



There is considerable uncertainty in the enthalpy of formation for  $SF_4Cl^+$ ; the value used is  $+327$  kJ mol<sup>-1</sup>, an upper limit determined from the appearance energy (AE) of  $SF_4Cl^+$  ions following dissociative photoionization of  $SF_5Cl$ .<sup>7</sup> The enthalpy of reaction (3) is expected to be less than the AE( $F^-$ ) of 12.7 eV, but the value for  $\Delta_r H^\circ_{298}$  ( $SF_3Cl^+$ ) is not known. It is noted that  $SF_3Cl^+$  was *not* observed in the photon or electron dissociative ionization experiments,<sup>7</sup> suggesting that the production of  $F^-$  from reaction (3) is unlikely. The increase in gradient of the cross section at 13.6 eV giving rise to feature 2 may correlate to production of  $F^-$  by reaction (4):



The thermochemical evidence therefore suggests that the most significant contribution to the  $F^-$  cross section at 14.06 eV is from production of the the  $F^- + SF_4^+$  ion pair in which the S–Cl bond is also broken, and not from reactions (1)–(3).

It is difficult to assign features in ion-pair spectra to specific dissociation reactions with any confidence. This is particularly true at higher photon energies because the number of accessible ion-pair products

increases. Some examples of the many reactions producing  $F^-$  which may be occurring at photon energies above 14 eV (giving rise to features 3–8, Figure 2(c)) are listed below:



Feature 1 of the  $F^-$  ion yield exhibits characteristics often associated with *direct* ion-pair formation; the onset is gradual and the resulting feature is broad and structureless.<sup>24</sup> Features 2–9 show characteristics usually associated with *indirect* ion-pair formation *via* crossing of a resonantly-excited Rydberg of  $SF_5Cl$  by an ion-pair potential curve. Assuming that these features do indeed arise from an indirect process, they have been assigned to Rydberg states of  $SF_5Cl$ , using the Rydberg formula for the energy levels,  $E_n$ , of a Rydberg series

$$E_n = IE - \frac{R_H}{(n-\delta)^2} \quad (II)$$

The results are shown in Table 1. These data assume that, in most cases, the given Rydberg state converges towards the excited state of  $SF_5Cl^+$  closest in energy to that of the resonance. For example, it is assumed that feature 2 at 14.06 eV converges to  $SF_5Cl^+$  ( $A^2A_1$ ) at 14.79 eV, and not to  $SF_5Cl^+$  ( $B^2A_2$ ) at 15.35 eV. The maximum cross section for  $F^-$  formation at 14.06 eV is  $6.1 \times 10^{-20} \text{ cm}^2$ . The higher-energy peaks are

much weaker with cross sections approximately one order of magnitude smaller; the cross section at 23.2 eV, corresponding to feature 6, is  $5.9 \times 10^{-21} \text{ cm}^2$ . This large difference may be due to the nature of the Rydberg state assigned to feature 2. Gaussian 03 calculations have shown that the  $A^2A_1$  state of  $\text{SF}_5\text{Cl}^+$  involves the removal of an electron from the  $15a_1$  molecular orbital which has both S–F<sub>eq</sub> and S–Cl bonding character;<sup>9</sup> the Rydberg state represented by feature 2 is thought to converge to the first excited state of  $\text{SF}_5\text{Cl}^+$ , and has been identified to come from reaction (4) where a fluorine anion and a chlorine atom are both cleaved from the molecule. However, it is not known unambiguously whether the F<sup>−</sup> signal comes from one of the four equivalent S–F(equatorial) bonds, as suspected, or from the S–F(axial) bond.

## 4.2 Formation of Cl<sup>−</sup>

Cl<sup>−</sup> anions were observed following VUV photoexcitation of  $\text{SF}_5\text{Cl}$ , but the signal was much weaker. Only one peak at 10.9 eV was detected in the range 8–35 eV (Figure 3). This feature was reproducible when scanning over the same energy region using a lithium fluoride window transmitting only  $h\nu < 11.8 \text{ eV}$ , and so it is not an artefact arising from higher-order radiation. The appearance energy of Cl<sup>−</sup> is  $10.6 \pm 0.2 \text{ eV}$ . Now, unlike the F<sup>−</sup> signals, these energies lie *below* the adiabatic ionization energy of  $\text{SF}_5\text{Cl}$ , 12.3 eV.<sup>6,7</sup> Therefore, Cl<sup>−</sup> can only form from an ion-pair dissociation, and this was confirmed by a linear dependence of Cl<sup>−</sup> signal with sample pressure. The only energetically accessible ion-pair reaction at this energy is:



The experimental onset therefore occurs 1.9 eV above the thermochemical threshold. The sharp onset implies that this ion-pair product forms indirectly.<sup>24</sup> This feature can be assigned to the resonant transition from the highest-occupied MO of  $\text{SF}_5\text{Cl}$  to the  $4p$  Rydberg state converging on  $\text{SF}_5\text{Cl}^+ X^2E$  which then predissociates into the  $\text{Cl}^- + \text{SF}_5^+$  ion-pair state. The quantum defect of this  $(9e)^{-1}4p$  Rydberg state is then calculated to be 1.47, consistent with data for high-lying Rydberg states (Table 1). The Cl<sup>−</sup> ion yield in Figure 3 could not be put accurately onto an absolute scale because the signal level was weak. However, by comparison of the signal-to-noise ratio of the Cl<sup>−</sup> spectrum with that of weak anions observed in other

studies of non-symmetric molecules where different bonds can break,<sup>30,31</sup> it is estimated that the maximum cross section for  $\text{Cl}^-$  production is less than *ca.*  $10^{-22} \text{ cm}^2$ . An upper limit for the bond dissociation energy of A–B in the generic ion-pair reaction  $\text{AB} \rightarrow \text{C}^- + \text{D}^+$  (+ neutral(s)) can be obtained from the anion appearance energy data (eq. (I)).<sup>24,30,31</sup> Using  $\text{AE}(\text{F}^-) = 12.7 \pm 0.2 \text{ eV}$ , an upper limit for  $D_o(\text{ClF}_4\text{S–F})$  of 4.82 eV is obtained. Likewise, using  $\text{AE}(\text{Cl}^-) = 10.6 \pm 0.2 \text{ eV}$ , an upper limit for  $D_o(\text{F}_5\text{S–Cl})$  of 4.44 eV is obtained. These upper-limit values are consistent with the thermochemically-determined bond dissociation energies of 3.70 and 2.54 eV for cleavage of the S–F and S–Cl bonds, respectively, in  $\text{SF}_5\text{Cl}$ .<sup>11,26,28</sup>

### 4.3 Formation of $\text{SF}_5^-$

$\text{SF}_5^-$  anions were also detected from  $\text{SF}_5\text{Cl}$  in the photon range of 12–35 eV (Figure 4). The signal was very weak, and again no attempt has been made to determine its absolute cross section. There is only one peak in the spectrum at 22.0 eV, and when the excitation source was fixed at this energy the  $\text{SF}_5^-$  signal was shown to increase *non-linearly* with increasing  $\text{SF}_5\text{Cl}$  gas pressure. Whilst a quadratic dependence of signal with pressure could not unambiguously be determined, we conclude that the  $\text{SF}_5^-$  anions are produced by dissociative electron attachment (see Section 2). This anion is the dominant species formed from thermal electron attachment to  $\text{SF}_5\text{Cl}$ .<sup>12,13</sup> As stated earlier, the thermal electron attachment rate coefficient for  $\text{SF}_5\text{Cl}$  lies between  $(2\text{--}5) \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ . This value is of a similar magnitude to that of other molecules such as  $\text{SF}_5\text{CF}_3$  ( $k_a = 8.0 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ) and  $\text{CF}_3\text{Br}$  ( $k_a = 1.4 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ ).<sup>32,33</sup> In photon-induced experiments, the anions  $\text{SF}_5^-$  and  $\text{Br}^-$  from  $\text{SF}_5\text{CF}_3$  and  $\text{CF}_3\text{Br}$ , respectively, are observed and identified as products from electron attachment reactions rather than from ion-pair dissociation.<sup>19,30</sup> Thus,  $\text{SF}_5\text{Cl}$  is following the same pattern. It is predicted that an anion spectrum resulting from an electron attachment process will mimic, at least to some extent, a threshold photoelectron spectrum.<sup>19</sup> The peak in Figure 4 at 22.0 eV matches the vertical ionization energy of a band observed by photoelectron spectroscopy at 21.9 eV, ionization to  $\text{SF}_5\text{Cl}^+ K^2E$  (see Figure 1). This is, however, the only such similarity between the two spectra, and the reasons are unknown.

## 5. Discussion and Conclusions

The anions  $F^-$ ,  $Cl^-$ , and  $SF_5^-$  have been observed following VUV photoexcitation of  $SF_5Cl$ .  $F^-$  and  $Cl^-$  arise from ion-pair dissociation,  $SF_5^-$  from dissociative electron attachment. Only the  $F^-$  spectrum can with confidence be put onto an absolute cross section scale, but the quantum yield for its production cannot be determined because photoabsorption cross section data are not available. Indeed, the analysis of the results is limited by the lack of other complementary spectroscopic investigations, *e.g.* fluorescence excitation as well as absorption spectra. Data for  $SF_5Cl$  are compared with that for comparable molecules in Table 2. It is an apparent coincidence that the  $AE(F^-)$  from both  $SF_5Cl$  and  $SF_6$  takes the same value,  $12.7 \pm 0.2$  eV. It is the relative position of the AE to the adiabatic ionization energy (AIE) of the parent molecule which is more interesting. The most significant features in the  $F^-$  spectrum from  $SF_6$  appear below its AIE,<sup>2,19</sup> yet for  $SF_5Cl$  the  $AE(F^-)$  and the first  $F^-$  peak exceed the AIE. The same comment can be made when comparing  $F^-$  from  $CF_4$  with  $F^-$  from  $CF_3Cl$ ;<sup>19,20,30</sup> for  $CF_4$  the  $AE(F^-)$  is less than the adiabatic IE, whereas for  $CF_3Cl$  the  $AE(F^-)$  exceeds the adiabatic IE (Table 2).  $SF_6$  and  $CF_4$  follow the expected trend that the probability for an excited electronic state to predissociate into ion pairs is greater in the absence of a competing autoionization process. It is possible, therefore, that the change in symmetry on substituting a fluorine for a chlorine atom (*e.g.*  $SF_6 \rightarrow SF_5Cl$ ) suppresses the formation of ion pairs below the ionization energy, or possibly increases the probability of a competing process such as neutral dissociation (*e.g.*  $SF_5Cl \rightarrow SF_5 + Cl$ ). We note that when comparing data for ion-pair formation from  $CF_3Cl$  with photoabsorption and fluorescence excitation spectra,<sup>30</sup> the evidence suggests that photoexcitation below the ionization energy almost exclusively results in neutral photodissociation.

The absence of ion-pair reactions from  $SF_5Cl$  producing  $Cl^-$  anions with any significant yield cannot easily be explained. Indeed, perhaps the most interesting aspect of this work is the observation that the  $F^-$  cross sections are at least two orders of magnitude greater than those for production of  $Cl^-$ , yet the S–Cl bond is

significantly weaker than the S–F bond ; the bond dissociation energies of the S–Cl and S–F bonds are 2.54 and 3.70 eV, respectively. Thus not only is the thermochemical energy of the product exit channel  $F^- + SF_4Cl^+$  *ca.* 2.8 eV higher than that for production of  $Cl^- + SF_5^+$ ,<sup>34</sup> there is also a much higher branching ratio at the appropriate energy for  $F^-$  than for  $Cl^-$  production. It appears that the dynamics of the crossing of Rydberg states with the ion-pair continuum determines the relative intensities of the anions that are formed, and not the thermochemistry of the different dissociation channels or the physical properties (*e.g.* electron affinity, electronegativity or polarizability) of the corresponding neutral species.

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**Table 1.** Rydberg assignments to features observed in the  $F^-$  ion yield recorded following the photoexcitation of  $SF_5Cl$ .

Feature <sup>a</sup>	E / eV <sup>b</sup>	IE <sup>c</sup>	$\delta$ <sup>d</sup>	assignment <sup>e</sup>
2	14.06	14.79 ( $A^2A_1$ )	1.68	$(15a_1)^{-1} 6p$
3	16.8 <sub>0</sub>	18.07 ( $\tilde{F}^2A_1$ )	1.73	$(14a_1)^{-1} 5p$
4	20.6 <sub>5</sub>	21.0 ( $J^2A_1$ )	1.80	$(13a_1)^{-1} 8p$
		21.9 ( $K^2E$ )	1.70	$(5e)^{-1} 5p$
5	21.6 <sub>5</sub>	21.9 ( $K^2E$ )	1.62	$(5e)^{-1} 9p$
6	23.2 <sub>0</sub>	25.1 ( $L^2A_1$ )	1.33	$(12a_1)^{-1} 4p$
7	23.9 <sub>5</sub>	25.1 ( $L^2A_1$ )	1.56	$(12a_1)^{-1} 5p$
8	24.6 <sub>0</sub>	25.1 ( $L^2A_1$ )	1.78	$(12a_1)^{-1} 7p$

<sup>a</sup> The feature in the  $F^-$  ion yield as labelled in Figure 2.

<sup>b</sup> The photon energy of the feature identified from the spectra in Figure 2. The uncertainty in these values is estimated to be  $\pm 0.01$  eV for feature 2,  $\pm 0.1$  eV for features 3–8.

<sup>c</sup> The electronic state of  $SF_5Cl^+$  to which the assigned Rydberg state converges. Values of the vertical ionization energy are taken from DeKock *et al.*<sup>6</sup>

<sup>d</sup> Value of the quantum defect calculated from the Rydberg formula, eq. (II).

<sup>e</sup> Rydberg orbital assignment. The numbering scheme for the MOs of  $SF_5Cl$  (Figure 1) is that used by Klyagina *et al.* and Parkes,<sup>8,9</sup> where both core and valence orbitals are counted.

**Table 2.** Comparison of data obtained for ion-pair formation of  $F^-$  from  $SF_5Cl$ ,  $SF_6$  and  $SF_5CF_3$ . A separate comparison for  $CF_3Cl$  and  $CF_4$  is also included.

Molecule	AIE <sup>a</sup> / eV	AE ( $F^-$ ) <sup>b</sup> / eV	Reaction at AE <sup>c</sup>	E ( $\sigma_{max}$ ) <sup>d</sup> / eV	Reaction at $\sigma_{max}$ <sup>c</sup>
$SF_5Cl$	12.3	$12.7 \pm 0.2$	not known	14.06	$SF_5Cl \rightarrow F^- + SF_4^+ + Cl$
$SF_6$	15.1	$12.7 \pm 0.2$	$SF_6 \rightarrow F^- + SF_5^+$	14.2	$SF_6 \rightarrow F^- + SF_5^+$
$SF_5CF_3$	12.9	$11.05 \pm 0.05$	$SF_5CF_3 \rightarrow F^- + CF_3^+ + SF_4$	16.9	not known
$CF_3Cl$	12.4	$16.0 \pm 0.2$	$CF_3Cl \rightarrow F^- + CF_2^+ + Cl$	21.0	not known
$CF_4$	15.4	$13.0 \pm 0.2$	$CF_4 \rightarrow F^- + CF_3^+$	14.0	$CF_4 \rightarrow F^- + CF_3^+$

<sup>a</sup> Adiabatic ionization energy for  $SF_5Cl$ ,<sup>6,7</sup>  $SF_6$ ,<sup>35</sup>  $SF_5CF_3$ ,<sup>29</sup>  $CF_3Cl$ ,<sup>36</sup> and  $CF_4$ .<sup>37</sup>

<sup>b</sup> Experimentally-observed appearance energy of  $F^-$  anions.

<sup>c</sup> The ion-pair reactions are assigned by comparing calculated enthalpies of reaction with onsets to features observed in the anion ion yield spectra.

<sup>d</sup> The energy for maximum cross section for production of  $F^-$ .

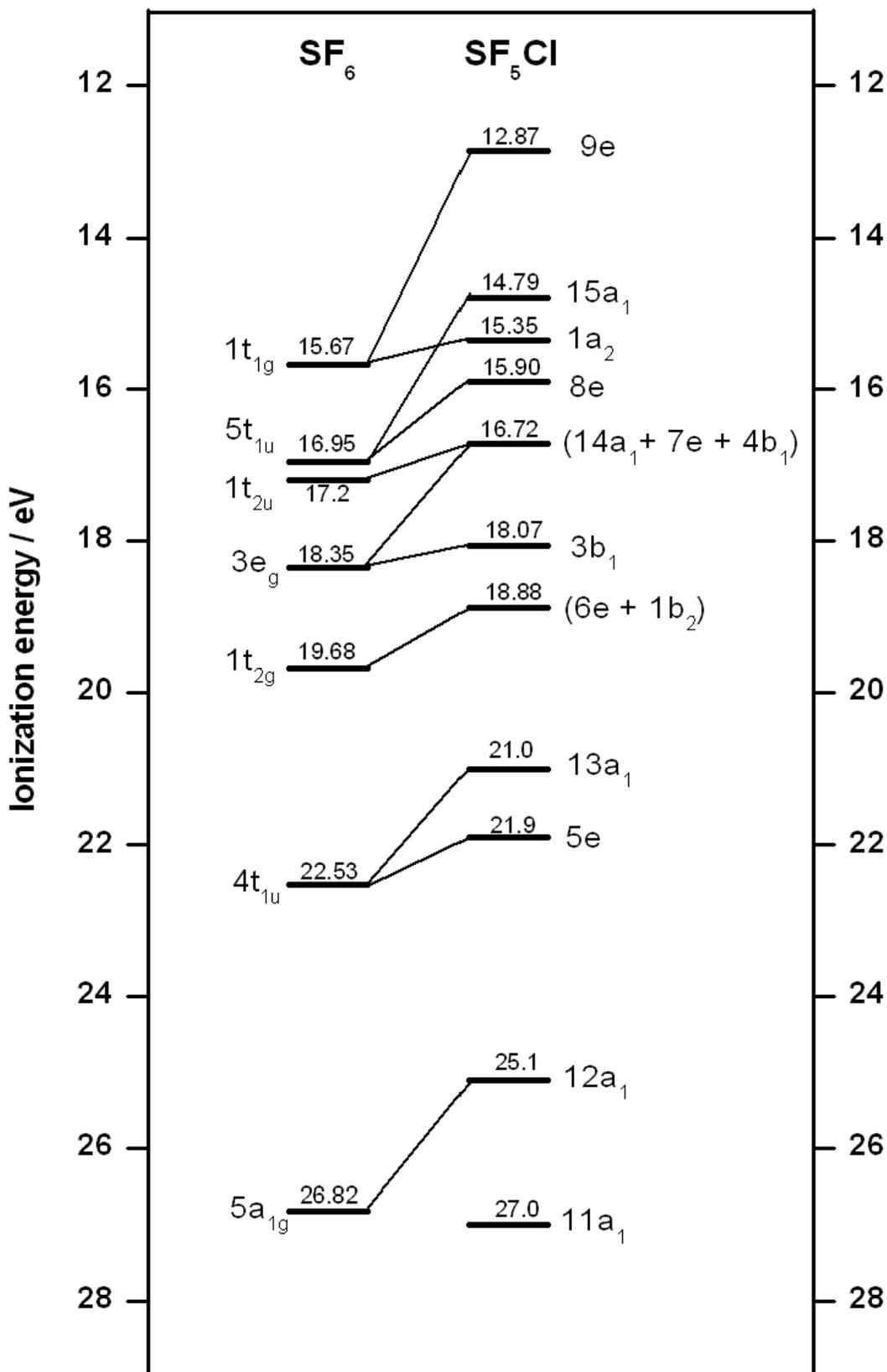
## ***FIGURE CAPTIONS***

**Figure 1** : Valence molecular orbitals (indicated by solid lines with numeric values in eV) assigned to energy maxima observed in experimental photoelectron spectra for SF<sub>6</sub> and SF<sub>5</sub>Cl.<sup>6,10</sup> Orbitals in brackets are thought to lie close in energy, but have not been resolved in experimental spectra.

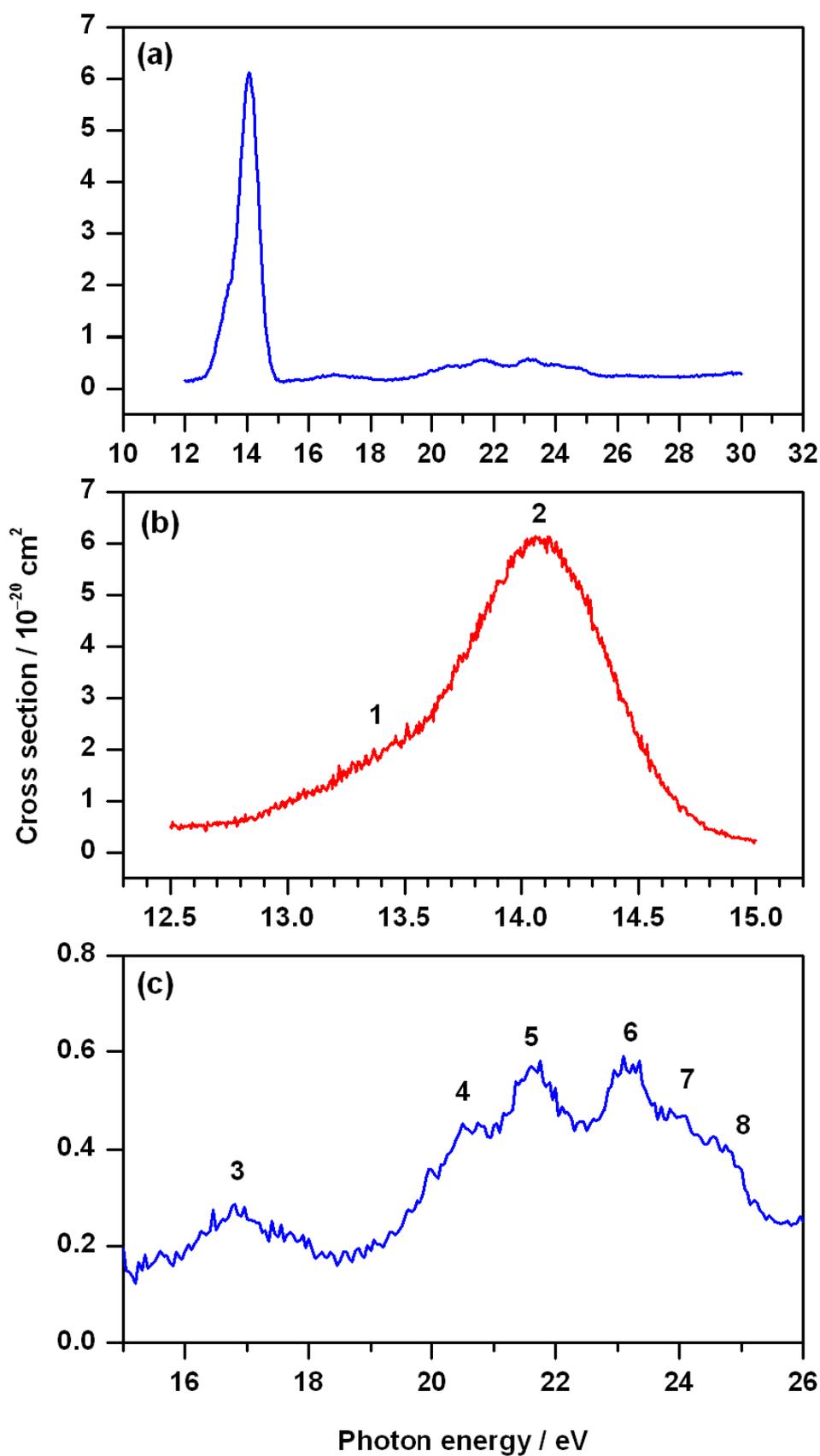
**Figure 2** : Upper-limit cross section for F<sup>-</sup> formation from SF<sub>5</sub>Cl; (a) from 12–30 eV recorded with a step size of 0.05 eV and a wavelength resolution of 6 Å, (b) from 12.5–15.0 eV recorded with a step size of 0.005 eV and a wavelength resolution of 1.2 Å, and (c) an expansion of (a) from 15–26 eV. All the features labelled 1–8 in spectra (b) and (c) are referred to in the text.

**Figure 3** : Ion yield of Cl<sup>-</sup> following photoexcitation of SF<sub>5</sub>Cl in the range 8–15 eV. The spectrum was recorded with a step size of 0.1 eV and a wavelength resolution of 6 Å.

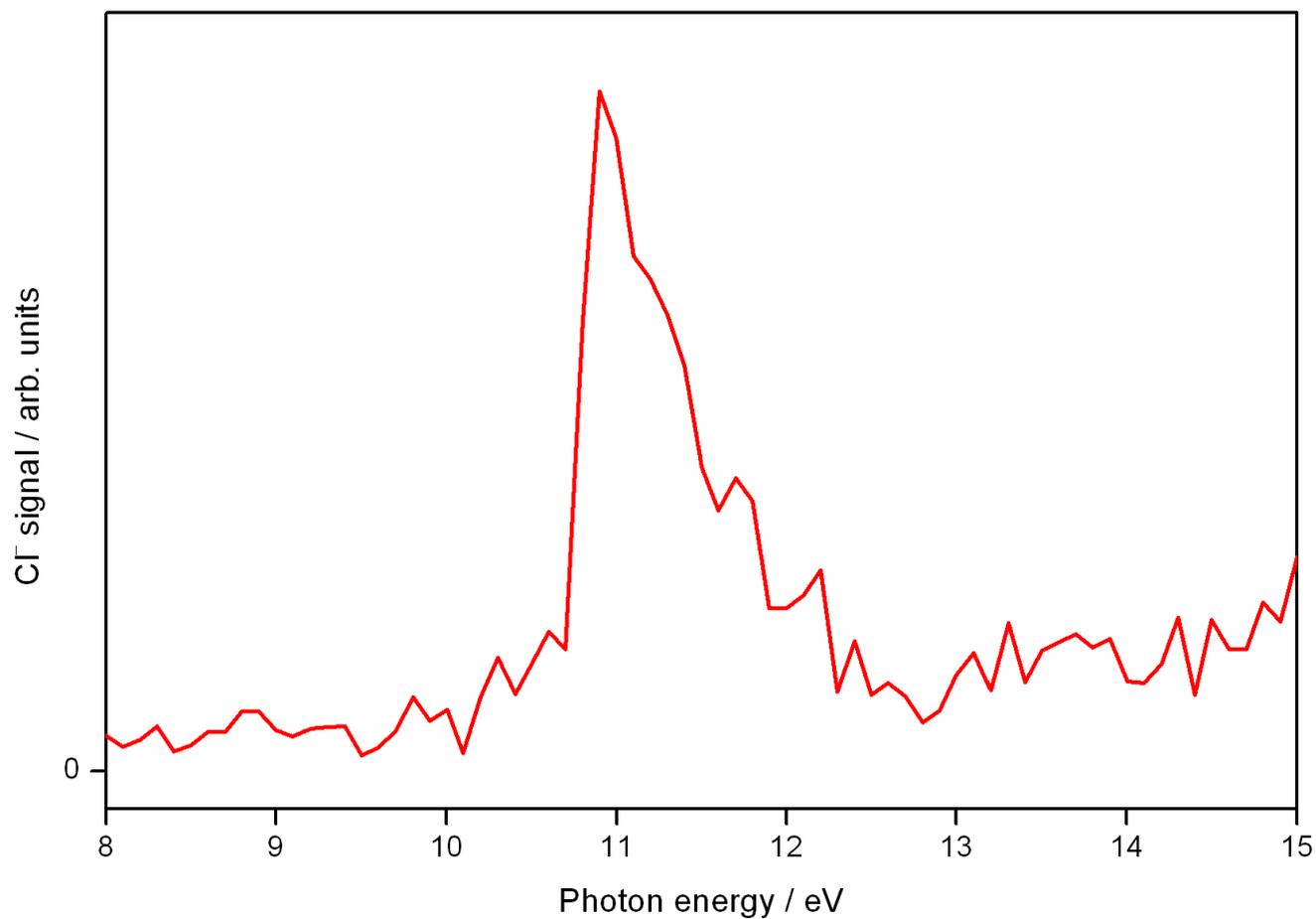
**Figure 4** : Ion yield of SF<sub>5</sub><sup>-</sup> following the photoexcitation of SF<sub>5</sub>Cl in the range 12–35 eV. The spectrum was recorded with a step size of 0.1 eV and a wavelength resolution of 6 Å.



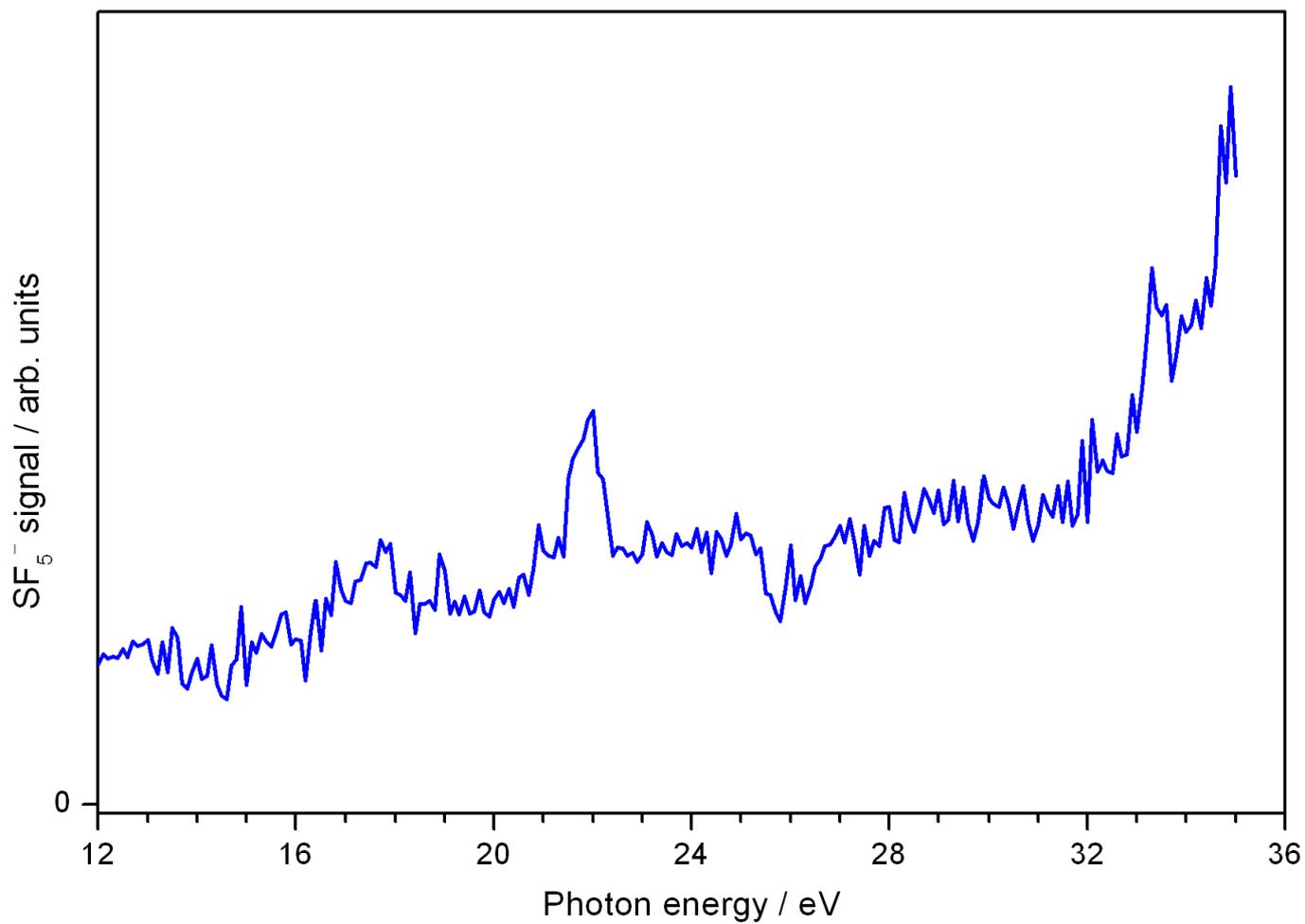
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## Graphic for Table of Contents

