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Vacuum-UV negative photoion spectroscopy of SF₅CI (Reference jp-2010-05597v : June 28, 2010)

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Using vacuum-UV radiation from a synchrotron, gas-phase negative ions are detected by mass spectrometry following photoexcitation of SF₅Cl. F⁻, Cl⁻ and SF₅⁻ are observed, and their ion yields recorded in the range 8–30 eV. F⁻ and Cl⁻ show a linear dependence of signal with pressure, showing that they arise from unimolecular ion-pair dissociation, generically written AB + hv \rightarrow C⁻ + D⁺ (+ neutral(s)). F⁻ is the strongest signal, and absolute cross sections are determined by calibrating the signal intensity with that of F⁻ from SF₆ and CF₄. Resonances are observed, and assigned to transitions to Rydberg states of SF₅Cl. The Cl⁻ signal is much weaker, despite the S–Cl bond being significantly weaker than the S–F bond. Appearance energies for F⁻ and Cl⁻ of 12.7 ± 0.2 and 10.6 ± 0.2 eV are determined. The spectra suggest that these ions form indirectly by crossing of Rydberg states of SF₅Cl 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, SF₆, involving production of cations, and chemical reactions,¹⁻³ but relatively few of the derivative molecule sulfur chloropentafluoride, SF₅Cl. The structure of SF₅Cl, C_{4v} symmetry in the gas phase, has been established by microwave spectroscopy⁴ and electron diffraction.⁵ 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 ⁶ and one using tunable vacuum-UV (VUV) photons coupled with threshold electron detection.⁷ The relative ordering of the valence molecular orbitals (MO) has been calculated using selfconsistent discrete variational X α methods.⁸ The state-selected fragmentation dynamics of the electronic states of SF_5Cl^+ has been studied by threshold photoelectron photoion coincidence spectroscopy.⁷ This publication also reported results from a Gaussian 03 calculation ⁹ which supported the MO assignments made by Klyagina et al.⁸ Figure 1 summarises the combined findings of these investigations, and correlates the MOs for SF₅Cl with those of SF₆ of O_h symmetry. While the ordering of the valence MOs in for SF₆ is well established,¹⁰ we note that the ordering and assignments given for SF₅Cl are based on more limited evidence. The kinetics and ionic products of the reactions of a large number of small cations with SF₅Cl have been studied in a selected ion flow tube.¹¹

The studies of anion production following excitation of SF₅Cl are even more limited. There have been two measurements of the thermal electron attachment rate coefficient to SF₅Cl : $(4.8\pm1.2) \times 10^{-8}$ cm³ s⁻¹ by van Doren *et al.*¹² and $(2.0\pm0.3) \times 10^{-8}$ cm³ s⁻¹ by Mayhew *et al.*,¹³ a factor of *ca.* 5–12 slower than the value for SF₆, $(2.38\pm0.15) \times 10^{-7}$ cm³ s⁻¹.¹⁴ Under thermal electron conditions, electron attachment to SF₅Cl is dissociative, producing SF₅⁻ (92%), Cl⁻ (5%) and FCl⁻ (3%), whereas that to SF₆ is predominantly non-dissociative. A recent crossed beam study of SF₅Cl with low-energy electrons in the range 0–14 eV ¹⁵ has clarified inconsistencies arising from two earlier studies.^{16,17} As in the thermal experiment, electron attachment is dissociative with SF₅⁻ 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.¹⁸

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 .¹⁹ 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 ,^{2,20} 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,²¹ 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.²² 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.²³ These signals are then put onto an absolute scale by determining the F^- intensity in the experiment from SF₆ and CF₄, and calibrating them to values of the cross section determined by Mitsuke *et al.* for SF₆ ((7 ±2) × 10⁻²¹ cm² at 14.3 eV) and CF₄ ((1.25±0.25) × 10⁻²¹ cm² at 13.9 eV.^{2,20} We estimate that the cross sections are accurate to a factor of *ca.* 2. F^- , CI⁻ and SF₅⁻ were the only anions detected. The variation of anion signal with pressure was determined for all three anions over the range *ca.* (0.5–5.0) × 10⁻⁵ mbar. F^- and CI⁻ 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 + hv \rightarrow C⁻ + D⁺ (+ neutral(s)). SF₅⁻ shows a non-linear dependence with pressure, with the signal rising more rapidly with pressure than from a linear relationship. This suggests that SF₅⁻ likely results from the two-step process of dissociative electron attachment. That is, SF₅Cl + hv \rightarrow SF₅Cl⁺ + e⁻, followed by SF₅Cl + e⁻ \rightarrow SF₅⁻ + Cl, where a quadratic dependence of SF₅⁻ signal with pressure is predicted.

The SF₅Cl sample was provided by Apollo Scientific with a quoted purity of *ca*. 97%. Impurities of SF₄, FCl and Cl₂ have been noted in previous studies using SF₅Cl samples, and small amounts of SF_xO_y species have also been detected – identified as by-products in the industrial production of SF₅Cl from the hydrolysis of SF₄.^{7,14} The effect of any contributions from these impurities to the anion spectra cannot be quantified, but is probably very small. Production of F⁻ from SF₄ and FCl is likely to be the biggest contaminent, so the values of the cross section for F⁻ production from SF₅Cl (Section 4.1 and Figure 2) are upper limits.

3. Thermochemistry

This work determines appearance energies at 298 K (AE₂₉₈) for fragment anions formed from photoexcitation of SF₅Cl, 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 AE₂₉₈ of an anion.²⁴ For the generic ion-pair reaction AB + hv \rightarrow C⁻ + D⁺ (+ neutrals(s)), this inequality can be written:

$$AE(C^{-}) \ge D_{o}(A-B) + IE(C) - EA(D)$$
(I)

where D_o is a bond dissociation energy, IE an ionisation energy and EA an electron affinity. Furthermore, in comparing AE₂₉₈ values with calculated enthalpies of appropriate dissociation reactions at 298 K, $\Delta_r H^o{}_{298}$, 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 AE₂₉₈ value cannot be equated to $\Delta_r H^o{}_{298}$ because of thermal effects,²⁵ the corrections needed to the AE₂₉₈ 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 Δn is the stoichiometric number of product species minus the number of reactant species. This is justified because the $|\Delta_r H^o{}_{298}|$ values are all large.

Values for $\Delta_r H^o_{298}$ of relevant ion-pair reactions were calculated using literature values for enthalpies of formation ($\Delta_f H^o_{298}$ in kJ mol⁻¹): SF₅Cl = -1039, SF₄Cl = -761, SF₅ = -915, SF₄ = -768, SF₃ = -442, SF₂ = -295, FCl = -50, Cl = +121, F = +79; SF₅⁻ = -1282, Cl⁻ = -227, F⁻ = -249; SF₄Cl⁺ ≤ +327, SF₅⁺ = +29, SF₄⁺ = +389, SF₃⁺ = +361, SF₂⁺ = +693, SF⁺ = +998, Cl⁺ = +1372.^{7,11,26-29} 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, F^- , Cl^- and SF_5^- , were detected following VUV photoexcitation of SF_5Cl . The F^- signal was by far the strongest, followed by Cl^- , whilst SF_5^- was only just detected above the sensitivity limit of the apparatus. The strength of the F^- signal may initially appear somewhat surprising, given that the F₄ClS–F bond dissociation energy, 3.70 eV, is stronger than that of F_5S –Cl, 2.54 eV.^{11,26,28}

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 SF₅Cl gas pressure, indicating it is formed *via* unimolecular ion-pair dissociation. The onset for F⁻ production is 12.7 ± 0.2 eV (Figure 2(b)), and we note that this value lies *above* the adiabatic ionization energy for SF₅Cl, 12.3 eV.^{6,7} 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 6.1×10^{-20} cm² 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:

$$SF_5Cl \rightarrow F^- + SF_4Cl^+ \qquad \Delta_r H^o{}_{298} \le 11.58 \text{ eV} \quad (1)$$

$$SF_5Cl \rightarrow F^- + SF_3^+ + FCl \qquad \Delta_r H^o{}_{298} = 11.41 \text{ eV} \quad (2)$$

$$SF_5Cl \rightarrow F^- + SF_3Cl^+ + F \qquad \Delta_r H^o{}_{298} \text{ unknown} \quad (3)$$

There is considerable uncertainty in the enthalpy of formation for SF_4Cl^+ ; the value used is +327 kJ mol⁻¹, an upper limit determined from the appearance energy (AE) of SF_4Cl^+ ions following dissociative photoionization of SF_5Cl^7 . The enthalpy of reaction (3) is expected to be less than the AE(F⁻) of 12.7 eV, but the value for $\Delta_f H^{\circ}_{298}$ (SF_3Cl^+) is not known. It is noted that SF_3Cl^+ was *not* observed in the photon or electron dissociative ionization experiments,⁷ 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):

$$SF_5Cl \rightarrow F^- + SF_4^+ + Cl \qquad \Delta_r H^o_{298} = 13.47 \text{ eV}$$
 (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:

$SF_5Cl \rightarrow F^- + Cl^+ + SF_4$	$\Delta_r H^o{}_{298} = 14.52 \text{ eV}$	(5)
$SF_5Cl \rightarrow F^- + SF_2^+ + F + FCl$	$\Delta_r H^o{}_{298} = 15.67 \text{ eV}$	(6)
$SF_5Cl \rightarrow F^- + SF^+ + F_2 + FCl$	$\Delta_r H^o{}_{298} = 18.01 \text{ eV}$	(7)
$SF_5Cl \rightarrow F^- + SF_2^+ + 2F + Cl$	$\Delta_r H^o{}_{298} = 18.26 \text{ eV}$	(8)
$SF_5Cl \rightarrow F^- + Cl^+ + SF_3 + F$	$\Delta_r H^o{}_{298} = 18.64 \text{ eV}$	(9)
$SF_5Cl \longrightarrow F^- + Cl^+ + SF_2 + F_2$	$\Delta_r H^o{}_{298} = 19.35 \text{ eV}$	(10)
$SF_5Cl \rightarrow F^- + SF^+ + 2F + FCl$	$\Delta_r H^o{}_{298} = 19.65 \text{ eV}$	(11)
$SF_5Cl \rightarrow F^- + SF^+ + F_2 + F + Cl$	$\Delta_r H^o{}_{298} = 20.60 \text{ eV}$	(12)
$SF_5Cl \longrightarrow F^- + Cl^+ + SF_2 + 2F$	$\Delta_r H^o{}_{298} = 20.99 \text{ eV}$	(13)
$SF_5Cl \rightarrow F^- + SF^+ + 3F + Cl$	$\Delta_r H^o{}_{298} = 22.25 \text{ eV}$	(14)

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.²⁴ Features 2–9 show characteristics usually associated with *indirect* ion-pair formation *via* crossing of a resonantly-excited Rydberg of SF₅Cl 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 SF₅Cl, using the Rydberg formula for the energy levels, E_n , of a Rydberg series

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

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 6.1×10^{-20} cm². 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 5.9×10^{-21} cm². 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 SF₅Cl⁺ involves the removal of an electron from the 15a₁ molecular orbital which has both S–F_{eq} and S–Cl bonding character;⁹ the Rydberg state represented by feature 2 is thought to converge to the first excited state of SF₅Cl⁺, 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⁻ signal comes from one of the four equivalent S–F(equitorial) bonds, as suspected, or from the S–F(axial) bond.

4.2 Formation of Cl⁻

Cl⁻ anions were observed following VUV photoexcitation of SF₅Cl, 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 hv < 11.8 eV, and so it is not an artefact arising from higher-order radiation. The appearance energy of Cl⁻ is 10.6 ± 0.2 eV. Now, unlike the F⁻ signals, these energies lie *below* the adiabatic ionization energy of SF₅Cl, 12.3 eV.^{6,7} Therefore, Cl⁻ can only form from an ion-pair dissociation, and this was confirmed by a linear dependence of Cl⁻ signal with sample pressure. The only energetically accessible ion-pair reaction at this energy is:

$$SF_5Cl \to Cl^- + SF_5^+ \qquad \Delta_r H^{\circ}_{298} = 8.72 \text{ eV}$$
 (15)

The experimental onset therefore occurs 1.9 eV above the thermochemical threshold. The sharp onset implies that this ion-pair product forms indirectly.²⁴ This feature can be assigned to the resonant transition from the highest-occupied MO of SF₅Cl to the *4p* Rydberg state converging on SF₅Cl⁺ $X^{2}E$ which then predissociates into the Cl⁻ + SF₅⁺ ion-pair state. The quantum defect of this (*9e*)⁻¹4*p* Rydberg state is then calculated to be 1.47, consistent with data for high-lying Rydberg states (Table 1). The Cl⁻ 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⁻ spectrum with that of weak anions observed in other

studies of non-symmetric molecules where different bonds can break,^{30,31} it is estimated that the maximum cross section for Cl⁻ production is less than *ca*. 10^{-22} cm². An upper limit for the bond dissociation energy of A–B in the generic ion-pair reaction AB $\rightarrow C^- + D^+$ (+ neutral(s)) can be obtained from the anion appearance energy data (eq. (I)).^{24,30,31} Using AE(F⁻) = 12.7 ± 0.2 eV, an upper limit for D_o (ClF₄S–F) of 4.82 eV is obtained. Likewise, using AE(Cl⁻) = 10.6 ± 0.2 eV, an upper limit for D_o (F₅S–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 SF₅Cl.^{11,26,28}

4.3 Formation of SF₅⁻

 SF_5^- anions were also detected from SF_5Cl 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 SF_5^- signal was shown to increase non-linearly with increasing SF₅Cl gas pressure. Whilst a quadratic dependence of signal with pressure could not unambiguously be determined, we conclude that the SF₅⁻ anions are produced by dissociative electron attachment (see Section 2). This anion is the dominant species formed from thermal electron attachment to SF₅Cl.^{12,13} As stated earlier, the thermal electron attachment rate coefficient for SF₅Cl lies between $(2-5) \times 10^{-8}$ cm³ s⁻¹. This value is of a similar magnitude to that of other molecules such as SF₅CF₃ ($k_a = 8.0 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$) and CF₃Br ($k_a = 1.4 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$).^{32,33} In photon-induced experiments, the anions SF₅⁻ and Br⁻ from SF₅CF₃ and CF₃Br, respectively, are observed and identified as products from electron attachment reactions rather than from ion-pair dissociation.^{19,30} Thus, SF₅Cl 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.¹⁹ 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 $SF_5Cl^+K^2E$ (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 SF₅⁻ have been observed following VUV photoexcitation of SF₅Cl. F⁻ and Cl⁻ arise from ion-pair dissociation, SF₅⁻ 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 SF₅Cl and SF₆ takes the same value, 12.7 ± 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 SF₆ appear below its AIE,^{2,19} yet for SF₅Cl the AE(F^-) and the first F^- peak exceed the AIE. The same comment can be made when comparing F^- from CF₄ with F^- from CF₃Cl;^{19,20,30} for CF₄ the AE(F^-) is less than the adiabatic IE, whereas for CF₃Cl the AE(F^-) exceeds the adiabatic IE (Table 2). SF₆ and CF₄ 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 CF₃Cl with photoabsorption and fluorescence excitation spectra,³⁰ 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^- + SF₄Cl⁺ *ca.* 2.8 eV higher than that for production of Cl⁻ + SF₅⁺,³⁴ 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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Feature ^a	E / eV ^b	IE ^c	δ^{d}	assignment ^e
2	14.06	14.79 (A^2A_1)	1.68	$(15a_l)^{-1} 6p$
3	16.80	18.07 ($\tilde{F}^{2}A_{1}$)	1.73	$(14a_1)^{-1} 5p$
4 20.65	$21.0 (J^2 A_1)$	1.80	$(13a_I)^{-1} 8p$	
	20.05	21.9 (K ² E)	1.70	$(5e)^{-1} 5p$
5	21.65	21.9 ($K^{2}E$)	1.62	$(5e)^{-1} 9p$
6	23.20	25.1 (L^2A_1)	1.33	$(12a_1)^{-1} 4p$
7	23.95	25.1 (L^2A_1)	1.56	$(12a_I)^{-1}5p$
8	24.60	25.1 (L^2A_1)	1.78	$(12a_1)^{-1}$ 7p

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

^{*a*} The feature in the F^- ion yield as labelled in Figure 2.

^b The photon energy of the feature identified from the spectra in Figure 2. The uncertainty in these values is estimated to be ± 0.01 eV for feature 2, ± 0.1 eV for features 3–8.

^{*c*} 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.*⁶

^d Value of the quantum defect calculated from the Rydberg formula, eq. (II).

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

Table 2. Comparison of data obtained for ion-pair formation of F^- from SF₅Cl, SF₆ and SF₅CF₃. A separate comparison for CF₃Cl and CF₄ is also included.

Molecule	AIE ^a /eV	AE (F ⁻) ^b / eV	Reaction at AE ^c	$\mathrm{E}\left(\sigma_{max}\right)^{d}/\mathrm{eV}$	Reaction at σ_{max}^{c}
SF5Cl	12.3	12.7 ± 0.2	not known	14.06	$SF_5Cl \rightarrow F^- + SF_4^+ + Cl$
SF_6	15.1	12.7 ± 0.2	$SF_6 \rightarrow F^- + SF_5^+$	14.2	$SF_6 \rightarrow F^- + SF_5^+$
SF ₅ CF ₃	12.9	11.05 ± 0.05	$SF_5CF_3 \rightarrow F^- + CF_3^+ + SF_4$	16.9	not known
CF ₃ Cl	12.4	16.0 ± 0.2	$CF_3Cl \rightarrow F^- + CF_2^+ + Cl$	21.0	not known
CF ₄	15.4	13.0 ± 0.2	$CF_4 \rightarrow F^- + CF_3^+$	14.0	$CF_4 \rightarrow F^- + CF_3^+$

^{*a*} Adiabatic ionization energy for SF₅Cl,^{6,7} SF₆,³⁵ SF₅CF₃,²⁹ CF₃Cl,³⁶ and CF₄.³⁷

^b Experimentally-observed appearance energy of F⁻ anions.

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

^d 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_6 and SF_5Cl .^{6,10} 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^- formation from SF₅Cl; (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⁻ following photoexcitation of SF₅Cl 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_5^- following the photoexcitation of SF_5Cl 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.



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_6 and $SF_5Cl.^{6,10}$ 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^- formation from SF_5Cl ; (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^- following photoexcitation of SF_5Cl 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_5^- following the photoexcitation of SF_5Cl 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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