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Vacuum-UV negative photoion spectroscopy of gas-phase polyatomic molecules

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Vacuum-UV negative photoion spectroscopy of gas-phase polyatomic molecules

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This review describes recent experiments to detect anions following vacuum-UV photoexcitation of gas-phase polyatomic molecules. Using synchrotron radiation in the range 10–35 eV at a resolution down to 0.02 eV, negative ions formed are detected by mass spectrometry. The molecules studied in detail include CF₄, SF₆ and CH₄; the CF₃X series where X = Cl, Br, I; the CH₃Y series where Y = F, Cl, Br and SF₅Z where Z = CF₃, Cl. Spectra and raw data only are reported for other members of the CHₓFₙ, CHₓClₙ including CCl₄, and CFₓClₙ series where (x + y) = 4; and saturated and unsaturated members of the CₓHₓ and CₓFₓ series up to m = 3. Anions detected range from atomic species such as H⁻/C₀ through to heavier polyatomics such as SF₅⁻, C₁F₃ and CH₂Cl⁺. The majority of anions display a linear dependence of signal with pressure, showing that they arise from unimolecular ion-pair dissociation, generically written as ABC⁺hν → D⁻ + E⁺ + neutral(s). In a few cases, the anion signal increases much more rapidly than a linear dependence with pressure, suggesting that anions now form via a multi-step process, such as dissociative electron attachment. Cross-sections for ion-pair formation can be put on to an absolute scale by calibrating the signal strength with those of F⁻/C₀ from SF₆ and CF₄, although there are difficulties associated with the determination of H⁻ cross-sections from hydrogen-containing molecules unless this anion is dominant. Following normalisation to total vacuum-UV absorption cross-sections (where data are available), quantum yields for anion production are obtained. Cross-sections in the range ca. 10⁻²²–10⁻¹⁹ cm², and quantum yields in the range ca. 10⁻⁴–10⁻¹ are reported. This review describes the two ion-pair mechanisms of indirect and direct formation and their differing characteristics, and the properties needed for anion formation by dissociative electron attachment. From this huge quantity of data, attempts are made to rationalise the circumstances needed for favourable formation of anions, and which anions have the largest cross-section for their formation. Since most anions form indirectly via predissociation of an initially excited Rydberg state of the parent molecule by an ion-pair continuum, it appears that the dynamics of this curve crossing is the dominant process which determines which anions are formed preferentially. The thermochemistry of the different exit channels and the microscopic properties of the anion formed do not appear to be especially significant. Finally, for the reaction ABC⁺hν → A⁻⁺BC⁺, the appearance energy of A⁻ can be used to determine an upper limit to the bond dissociation energy of AB (to A + BC), or an upper limit to that of ABC⁺ (to A + BC⁺). Where known, the data are in excellent agreement with literature values.

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Keywords: ion-pair formation; anion; electron attachment; synchrotron; bond
dissociation energy

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1. Introduction
The production of an anion–cation pair of fragments following unimolecular dissociation
of an isolated gas-phase molecule is often called ‘ion-pair formation’. For a diatomic
molecule, AB, this reaction can generally be described as

\[ AB + hν \rightarrow A^- + B^+. \] (1)
For a polyatomic molecule, ABC, the ion-pair reaction may also produce neutral fragments,

\[ \text{ABC} + h\nu \rightarrow \text{A}^- + \text{BC}^+, \quad (2) \]

or

\[ \text{ABC} + h\nu \rightarrow \text{A}^- + \text{B}^+ + \text{C}. \quad (3) \]

This review is concerned exclusively with polyatomic molecules, so from henceforth we will use reactions (2) or (3) to describe a generic ion-pair reaction. In these studies, it is usually the anion, A\(^-\), that is detected as a function of the photon energy. Anions formed in this way can either form directly or indirectly, described fully in Section 2. An anion–cation pair may be formed by direct excitation to the ion-pair state, or indirectly via predissociation of an initially excited neutral state of ABC. Indirect formation is by far the more common mechanism, the excited neutral states are nearly always Rydberg in character, and so our experiments relate closely to the vacuum-UV absorption spectroscopy of Rydberg states of polyatomic molecules.

A\(^-\) can also be produced above the ionisation energy of the parent molecule by the alternative mechanism of dissociative electron attachment:

\[ \text{ABC} + h\nu \rightarrow \text{ABC}^+ + e^- \]

followed by

\[ \text{ABC} + e^- \rightarrow \text{A}^- + \text{BC} \quad \text{or} \quad \text{A}^- + \text{B} + \text{C}. \quad (4) \]

A more accurate description of this type of study is therefore ‘negative photoion spectroscopy’, this explains the title of this review, and one should regard ion-pair formation in a polyatomic molecule, (2) or (3), as a special case of negative photoion spectroscopy in which a cation is produced simultaneously. Furthermore, with ion-pair formation the signal of A\(^-\) increases linearly with the concentration or pressure of ABC, as only one molecule of parent is needed to produce one anion. By contrast, if A\(^-\) is produced by dissociative electron attachment, (4), then the A\(^-\) signal should increase quadratically with the concentration of ABC since two molecules of ABC are needed to produce one anion; at the very least, the rate of change of A\(^-\) signal will increase as the concentration of parent molecule increases. Whilst the formation of A\(^-\) by reaction (4) is also a multi-step indirect process, we will always describe this method of anion production as two-step dissociative electron attachment. This will avoid confusion with the indirect ion-pair reaction described above for production of an anion–cation pair by predissociation of a Rydberg state of ABC.

Typically, these reactions are endothermic by at least 8 eV, corresponding to a photon wavelength less than ca. 150 nm, with this energy increasing as the extent of fragmentation of the polyatomic molecule increases. Therefore, a photon in the vacuum-ultraviolet (VUV) region of the electromagnetic spectrum must be absorbed by the molecule, and it is no surprise that the majority of negative photoion studies of polyatomic molecules use tunable VUV radiation from a synchrotron as the source of electromagnetic radiation. For spectroscopic studies, the relatively poor resolution of such sources, compared to other sources such as VUV lasers, is more than compensated by the ease with which the photon energy can be tuned. For dynamical studies, radiation from a synchrotron can operate
either as a source of linearly or circularly polarised radiation, but such properties have received little attention to date in negative photoion or ion-pair studies.

For reaction (2), the appearance energy of the anion, \( AE(A^-) \) is constrained to the energetic relationship:

\[
AE(A^-) \geq D^0(A - BC) + IE(BC) - EA(A),
\]

where \( D^0 \) is a dissociation energy, \( IE \) an ionisation energy and \( EA \) an electron affinity. If experiments are performed at 298 K, then we can write:

\[
AE_{298}(A^-) \geq D^0_{298}(A - BC) + IE(BC) - EA(A).
\]

To avoid confusion about signs, we note that whilst the IE of a molecule is always positive (i.e. the reaction \( ABC \rightarrow ABC^+ + e^- \) is always endothermic), we use the convention used by most chemical physicists that a positive EA corresponds to the energy of \( A^- \) lying below that of \( A \) (i.e. the reaction \( A + e^- \rightarrow A^- \) is exothermic). As stated earlier, ion-pair production can either occur directly into the ion-pair continuum, or indirectly following predissociation of an initially excited Rydberg electronic state into the continuum. On Franck–Condon grounds the latter process is more common [1], so the detection of ion pairs provides information on the electronic structure of a molecule and the decay dynamics of its excited states.

An alternative way to express the inequality of Equation (I) is to write:

\[
AE(A^-) \geq IE(ABC) + D^0(A - BC^+) - EA(A).
\]

or

\[
AE_{298}(A^-) \geq IE(ABC) + D^0_{298}(A - BC^+) - EA(A).
\]

Thus, ion-pair formation may occur at energies below the adiabatic IE of ABC if the electron affinity of \( A \) exceeds the dissociation energy of \( A^-BC^+ \). Anions are then being detected in the absence of photoelectrons, facilitating the experiment. This condition is met for all the thallium halide diatomic molecules [2]. Furthermore, for \( \text{TlBr} \) and \( \text{TlI} \) the threshold for ion-pair formation occurs above the VUV onset of 200 nm, or below ca. 6 eV, making the detection of anions with conventional UV lamp sources relatively easy. Thus the study of the negative photoion spectroscopy of these molecules started as early as the 1930s. The halogen and inter-halogen diatomic molecules provide a rich source of ion-pair states, due to the relatively high EA value of all the halogen atoms. These molecules, reviewed in [3], could be studied by VUV and UV lasers operating in the wavelength range of ca. 150–250 nm (or 5–8 eV), and were complemented by synchrotron studies using VUV radiation from the second generation of these sources.

The first studies on polyatomic molecules in the 1960s, mostly from the National Bureau of Standards in Washington, DC, USA, used the continuum sources from discharge lamps coupled with mass spectrometric detection of the anion, but these studies rarely accessed wavelengths below 100 nm, or photon energies above 12.4 eV [4,5]. The first set of dedicated experiments on polyatomic molecules using VUV radiation from a synchrotron were made in the early 1990s by Mitsuke et al. [6–10] at the Institute of Molecular Sciences in Okasaki, Japan, and a range of molecules were studied including \( \text{CH}_4 \) and larger hydrocarbons, \( \text{CF}_4, \text{SF}_6 \) and \( \text{CH}_3X \) (\( X = \text{F, Cl, Br} \)). The state of knowledge of ion-pair states in diatomic and polyatomic molecules up to 1996 was reviewed by
A more recent project using a pulsed time-of-flight reflectron mass spectrometer to detect anions has been initiated by Tian et al. [11] at the National Synchrotron Radiation Laboratory in Hefei, China. Starting in the 1990s, the development of imaging techniques opened a new window into ion-pair spectroscopy. Coupled with linearly polarised VUV lasers, the dynamics of ion-pair dissociation via molecular Rydberg states started to be investigated, with detailed studies on CH$_3$Cl and CH$_3$Br being reported [12,13]. Simultaneously, the development of threshold ion-pair production spectroscopy [14,15] applied to diatomic and some hydride triatomic molecules meant that the full potential of laser-based coherent VUV sources at high resolution could be applied to ion-pair formation. These studies up to 2006 were reviewed by Suits and Hepburn [16].

In a series of experiments performed over the last 5 years, we have exploited the increased sensitivity of modern mass spectrometers and the wide tunability and availability of synchrotron sources over the energy range 10–30 eV to study anion formation from a range of polyatomic molecules. The systems studied include CH$_4$, CF$_4$, SF$_6$, CH$_3$X (X = F, Cl, Br), CF$_3$Y (Y = Cl, Br, I), SF$_2$Z (Z = Cl, CF$_3$), CH$_3$F$_x$ (x + y = 4), CH$_3$Cl$_b$ (a + b = 4), CF$_x$Cl$_d$ (c + d = 4), C$_m$H$_n$ and C$_m$F$_n$ (m = 1, 2, 3) [17–22]. For common molecules studied, a much wider range of anions are observed than those observed by Mitsuke et al., and we have developed a generic methodology to determine absolute cross-sections and quantum yields for anion formation; this has never been done before for such a wide range of molecules. Our data form the most comprehensive collection of information on ion-pair formation in polyatomic molecules since the Berkowitz review [1]. Perhaps more than other reviews on ion-pair formation, here we attempt to explain why some anions form in preference to others. Since many of our studies involve fluorinated molecules, it is perhaps not surprising that phenomena such as the electronegativity of the departing anion and the perfluoro effect [23] can explain some of the observations. However, certainly for indirect ion-pair formation, it is the dynamics of the crossing between the Rydberg and the ion-pair states which determine predominantly the product anions that are formed.

2. Direct and indirect ion-pair formation, Rydberg states

In their review on halogen diatomic molecules, Lawley and Donovan [3] suggest a model for the potential energy function of an ion-pair state, incorporating an exponential repulsion term with a long-range Coulombic attractive interaction,

$$V(r) = A \exp(-\alpha r) - \frac{e^2}{4\pi\varepsilon_0 r} + E_{ip},$$

where $V(r)$ is the potential energy, $r$ the bond distance along the reaction coordinate, $A$ and $\alpha$ are constants and $E_{ip}$ is the energy needed to place $V(r)$ onto an absolute scale. For reaction (1), $E_{ip} = D'(A - B) + I(E(B) - E(A))$. This model assumes both pure ionic behaviour and the equilibrium bond distance of the ion-pair state at equilibrium being large.

As stated in Section 1, an anion–cation pair may be formed by direct excitation to the ion-pair state, or indirectly via predissociation of an initially excited neutral state. Figure 1 shows these two processes for the generic polyatomic molecule ABC dissociating into $A^- + BC^+$. Direct ion-pair formation involves excitation to the repulsive inner wall of the
potential energy surface above the asymptotic dissociation energy. Consequently, the transition may have very small Franck–Condon factor at threshold, and vibrational states of the ion-pair potential curve cannot be probed. However, given the necessary sensitivity in the experiment, unless the Franck–Condon factor is truly zero at threshold one would expect the signal of $A/C_0$ to turn on at its thermochemical energy. By contrast, for the indirect process the restricting factor is not this Franck–Condon overlap, but rather the degree of coupling between the initially excited neutral state and the ion-pair state. In addition, vibrational levels within the neutral excited state can be probed. Although it is not shown as such in Figure 1(b), there is now no reason why the signal of $A^-$ should turn on at its thermochemical threshold, because the initially excited neutral state may lie higher in energy than the $A/C_0 + BC^+$ threshold. This explains the inequality in the energetics of Equations (I)–(III). Nevertheless, regardless of which process leads to the formation of ion pairs, competing processes can result in products other than $A^- + BC^+$ being formed. These processes include neutral dissociation, molecular ionisation or fluorescence. The measurement of quantum yields for these different exit channels is notoriously difficult, especially in the VUV region of the spectrum where absolute standards can be difficult to obtain. However, the general acceptance is that the quantum yield for ion-pair formation in polyatomic molecules is small, typically $10^{-3}$ or less, with the value decreasing as the size of the molecule increases [1,16,24].

Figure 1 (colour online). (a) Potential energy ($V$) as a function of bond distance ($r$) showing direct ion-pair formation process for the generic reaction $ABC + h\nu \rightarrow A^- + BC^+$. $E_{ip}$ represents the asymptotic ion-pair dissociation energy. (b) Potential energy ($V$) as a function of bond distance ($r$) showing indirect ion-pair formation process via predissociation of a neutral excited state ($ABC^*$), i.e. $ABC + h\nu \rightarrow (ABC^*) \rightarrow A^- + BC^+$. 
Rydberg states are commonly identified as the initially excited intermediate involved in indirect ion-pair formation (i.e. ABC* in Figure 1(b)) [1,24]. A molecular Rydberg state is a high-lying electronic state of the neutral molecule where an electron is excited such that it observes the molecule as a distant positively charged core. The Rydberg electron resides in an atomic-like orbital which is very large compared to the size of the molecule. Series of Rydberg states converge to ionisation limits and generally obey the Rydberg formula [24,25]:

\[
E_n = \text{IE} - \left[ \frac{R_\infty}{(n - \delta)^2} \right],
\]

where \(E_n\) is the energy of the \(n\)th Rydberg state, \(\text{IE}\) is the ionisation energy to which the Rydberg series converges, \(R_\infty\) is the Rydberg constant (109737.32 cm\(^{-1}\) or 13.6059 eV, the IE of atomic hydrogen), \(n\) is the principal quantum number of the Rydberg orbital and \(\delta\) is the quantum defect. \((E_n - \text{IE})\) is called the term value. The angular momentum quantum number, \(l\), of the Rydberg orbital is identified by \(\delta\). For example, the value of \(\delta\) will be the same for each member of an \(ns\) (or \(np\) or \(nd\) ... etc.) Rydberg series. Typical values of \(\delta\) for period 1 and period 2 elements of the periodic table are: for \(ns\) series, 0.9–1.2; for \(np\) series, 0.3–0.6; for \(nd\) series, <0.1 [25]. In addition, \(\delta\) values increase with increasing period number. Thus, an \(np\) Rydberg orbital in Cl will have a larger quantum defect than an \(np\) Rydberg orbital in F. \(\delta\) therefore represents an arbitrary, dimensionless number, the magnitude of which reflects the degree of orbital-core penetration, including the shielding effects of ‘core’ electrons on the Rydberg electron. The Rydberg formula originated from the analysis of the spectrum of atomic hydrogen, a single-electron system with no requirement to define \(\delta\); in Equation (V), for atomic H \(\delta = 0\). The quantum defect is introduced for many-electron systems to account for electron–electron interactions. Thus, the smaller the value of \(\delta\), the more the system behaves like a hydrogen atom and the more diffuse the Rydberg orbital becomes.

Peaks in a spectrum (providing a value for \(E_n\)) may be assigned to a Rydberg orbital using the Rydberg formula if the value for the IE is known. In practice, it is common that several assignments exist for the same value of \(E_n\) because of many possible combinations for IE, \(n\) and \(\delta\). Assignments presented later are therefore given with a degree of uncertainty, reflecting the moderate resolution at which the negative photoion spectra are recorded. One particular difficulty in assigning molecular Rydberg orbitals is that only quantum defect values for atomic systems are well-known. In this work the tabulations by Theodosiou et al. [26] were used as a guide to identify appropriate quantum defect values. More confident assignments require \(E_n\) to be known more accurately from higher resolution spectra, or several peaks to be fitted to the same Rydberg series; the latter is more likely to be possible from total photoabsorption or atomic spectroscopy.

3. Thermochemical aspects of negative photoion or ion-pair spectroscopy

The standard enthalpy of a unimolecular reaction, \(\Delta_rH^F\), can be calculated if the standard enthalpies of formation (\(\Delta_fH^F\)) for each individual reactant and product
species are known. All our experiments are performed at 298 K, and thus the following relationship can be used:

$$
\Delta_r H^o_{298} = \sum \Delta_r H^o_{298}(\text{products}) - \sum \Delta_r H^o_{298}(\text{reactants}). \tag{VI}
$$

The $\Delta_r H^o_{298}$ values used to calculate these enthalpies of reaction are taken from standard sources [27,28], although more recent and accurate data may be available for some of the ion-pair products we observe. In reality, however, it is the change in standard Gibbs energy of the reaction, $\Delta_r G^o$, and not the change in standard enthalpy, which determines the thermodynamic feasibility of a reaction. The relationship between $\Delta_r G^o$ and $\Delta_r H^o$ is given by

$$
\Delta_r G^o = \Delta_r H^o - T \Delta_r S^o, \tag{VII}
$$

where $T$ is the temperature in K and $\Delta_r S^o$ is the standard entropy of reaction. Thus, the effects of entropy in a reaction are ignored when using enthalpy, and not free energy values. For most ion-pair reactions needing the input of a vacuum-UV photon (e.g. 10 eV ≈ ca. 965 kJ mol$^{-1}$), the $T \Delta_r S^o$ term is small compared to the magnitude of $\Delta_r G^o$ or $\Delta_r H^o$, even though $\Delta n$, the number of product minus the number of reactant species, for reactions (1)–(3) is always positive and never zero. We therefore believe that the use of $\Delta_r H^o$, the endothermicity of the reaction, instead of $\Delta_r G^o$ is justified, provided this fact is acknowledged. However, in the very few cases where $\Delta_r H^o$ is very small and $\Delta_r S^o$ is very large, this approximation may not be applicable. Note that for bimolecular reactions involving cations or anions, which are not considered in this review, $\Delta_r H^o$ values can be much smaller, and the magnitude of $T \Delta_r S^o$ may sometimes lie within the uncertainty of the calculated $\Delta_r H^o$ value. Then entropic effects may be significant.

We have seen already that the asymptotic ion-pair formation energy, $E_{ip}$, from a generic polyatomic molecule ABC can be expressed using either of the two equations:

$$
E_{ip}(A^- + BC^+) = D^o(A – BC) + \text{IE}(BC) – \text{EA}(A),
$$

or

$$
E_{ip}(A^- + BC^+) = \text{IE}(ABC) + D^o(A – BC^+) – \text{EA}(A). \tag{VIII}
$$

As seen earlier, one advantage of using the second of these two equations is to identify that ion-pair formation can occur at an energy below the onset to ionisation: $E_{ip} < \text{IE}$ when $\text{EA}(A) > D^o(A – BC^+)$. This is often the case when A is a halogen atom because their EA values are relatively large. Below the IE, any ion formed must arise as a result of an ion-pair reaction, and positive or negative species can be detected with relative ease. Above the IE, however, in addition to anions, cations and free electrons are produced often in huge excess, which provide additional experimental challenges.

In practice, the value of $E_{ip}$ is often not known or cannot be measured, and it is more convenient to use the experimental appearance energy instead. Although there are several definitions of the appearance energy in the literature, at the relatively modest resolution of our experiments, ca. 0.05–0.20 eV (see Section 4), we believe it most appropriate to define the $\text{AE}_T$ at the temperature of the experiment, $T$ (which is usually 298 K), as the lowest energy at which ion-pair formation is detected; that is, the photon energy at which an anion signal is first observed above the background noise. This can be considered as the
value for $\nu$ shown earlier in Figure 1(a) and (b). The two Equations (VIII) may then be re-written as the inequalities shown earlier in Equations (I)–(III). These inequalities can be used to calculate an upper limit to the value of either a bond dissociation energy or an ionisation energy, or a lower limit to the value of an electron affinity, whichever has the least well-known value [1,29].

We shall see that the anion detected is identified by its mass (Section 4). However, the positive ion and any neutral fragments produced by the ion-pair reaction are not known. The enthalpy change for a unimolecular ion-pair reaction may be calculated using Equation (VI) and compared with onsets to features in a spectrum. Previous experimental results from Mitsuke et al. showed that an experimental AE$_T$ value commonly occurs at, or slightly higher in energy than the calculated thermochemical threshold (i.e. the value for $E_{ip}$ calculated from Equation (VIII). Assigning an AE$_T$ value to a particular reaction is often straightforward, because usually only one ion-pair dissociation is energetically possible; for the lowest energy ion-pair process only one bond is broken and no neutral fragments are produced. Assigning a reaction to features in a spectrum at higher energy is often more difficult because many different ion-pair dissociation channels become energetically open.

The values calculated from the right-hand side of Equation (VI) are enthalpy changes. Before proceeding further, energy and enthalpy must be distinguished. We consider one molecule of an ideal gas interacting with a photon to produce a negative–positive pair of ions. The enthalpy change, $\Delta_r H^o$, does not allow for the fact that some internal energy is transferred to the surroundings as an increase in volume and/or pressure; the number of gaseous species increases due to the unimolecular dissociation reaction, $\Delta n > 0$, and the products are produced with translational momentum. The enthalpy change of a gas-phase reaction where all the species behave as ideal gases is defined by

$$\Delta_r H^o = \Delta_r U^o + RT \Delta n,$$

where $U$ is the internal energy and $R$ the universal gas constant. Energy and enthalpy are only equivalent quantities when $T=0$ or $\Delta n = 0$. Corrections to AE$_T$ values, so that they may be compared to those for $\Delta_r H^o_T$, have been outlined by Traeger and McLoughlin [30] for photoionisation reactions. For the generic ion-pair reaction $ABC + h\nu \rightarrow A^- + BC^+$ at 298 K, their methods can be modified to show that

$$\Delta_r H^o_{298} \leq \text{AE}_{298}(A^-) + \int_0^{298} c_{p,m}(A^-) \cdot dT + \int_0^{298} c_{p,m}(BC^+) \cdot dT - \frac{5}{2} RT, \quad (X)$$

where $c_{p,m}$ is a molar specific heat capacity at constant pressure. The upper limit for $\Delta_r H^o_{298}$ arises because the appearance energy of $A^-$ defines an upper limit to the thermochemical energy of $A^- + BC^+$. The inequality arises in the presence of a kinetic shift and/or a barrier in the exit channel, the equality holds if both effects are insignificant. Considering the second and third terms on the right-hand side of Equation (X),

$$\int_0^{298} c_{p,m}(A^- \text{ or BC}^+) \cdot dT = H^o_{298} - H^o_0. \quad (XI)$$

For both anion and cation, this term may contain contributions from translational ($2.5RT$), rotational (up to $1.5RT$) and vibrational ($N_A h\nu/\exp(h\nu/k_B T) - 1$ per mode) motion evaluated at $T=298$ K. For many neutral molecules where all its vibrational
frequencies are known, values of \((H_{o298}^o - H_{o}^o)\) are tabulated [27]. For some anions and cations, \textit{ab initio} calculations of vibrational frequencies may be necessary. In practice, however, unless the products of the reaction are large polyatomic species with many low-frequency vibrational modes contributing to their vibrational partition functions, the difference between \(\Delta_rH_{298}^o\) and \(\Delta E_{298}\) is relatively small, typically <0.1 eV or 10 kJ mol\(^{-1}\). This correction falls within the combination of uncertainties in the calculated \(\Delta_rH_{T}^o\) and \(\Delta E_{T}\) values determined in our work. In this work, the thermal correction is therefore ignored: experimental \textit{energy} values are compared like-for-like with calculated \textit{enthalpy} changes.

4. Experimental aspects

Data were collected at the second-generation Synchrotron Radiation Source (SRS), Daresbury, in the 2 years before its closure in the autumn of 2008. All experiments used the 1 m focal length Wadsworth monochromator on beamline 3.1 which was commissioned in 2004. This beamline has been described in detail elsewhere [31]. It was designed as a high-flux beamline operating at fairly moderate resolution for use in flux-limited experiments, with ease of tunability a high priority. Since vacuum-UV negative photoion spectroscopy is a flux-limited experiment, it might seem a strange choice of source to use for such experiments when superior beamlines, e.g. based on a VUV undulator, are available elsewhere in Europe. However, many of the VUV beamlines on third-generation European sources, e.g. Soleil in France, are based on undulators where tunability over a wide range of the VUV/XUV is not facile, or they operate at a much higher resolution, e.g. the Swiss Light Source VUV beamline, than is ideal for these experiments and their resolution cannot be degraded sufficiently to enhance the flux. In retrospect, therefore, we believe that the Daresbury source, despite its age, combined with a newly commissioned VUV monochromator designed for maximum flux at modest resolution was the ideal combination for these experiments. This beamline could operate over the range 8–35 eV, this energy range being provided by two gratings mounted back-to-back and interchangeable under vacuum. If there was sufficient flux to operate an experiment at high resolution, the best resolution attainable, determined by the size of the horizontal electron beam in the storage ring, was ca. 0.05 nm, corresponding to 0.004 eV at 10 eV or 0.016 eV at 20 eV. In practice, the monochromator was usually operated at an inferior resolution to enhance flux. The maximum flux output at the peak of the two lamellar gratings, ca. 60 and 120 nm or 20 and 10 eV, was approximately \(4 \times 10^{11}\) photons per second per 100 mA of stored beam current when operating at a bandwidth of 0.1% of the excitation wavelength [31]. All experiments were conducted using the pseudo-continuous-wave nature of the synchrotron beam.

The apparatus used for these negative photoion spectroscopic studies is shown in Figure 2. Before our experiments, it had been used to detect anions at higher photon energies above ca. 25 eV, and its operation in this mode is described elsewhere [32]. A 2 mm diameter, 300 mm long capillary light guide connected the beamline to the apparatus, focussing the monochromatised light directly into the interaction region. The light guide also provided the necessary differential pumping, ca. three orders of magnitude in pressure, between the beamline and the experiment. The gas under study is injected via a needle generating an effusive directed jet (with no internal cooling) which bisects
orthogonally the incident photon beam. The crossing point, which dictates the centre of the interaction region, is positioned in the middle of two grids on the third orthogonal axis. A potential difference across the grids sweeps negative ions along this axis towards a three-element electrostatic lens for focussing, and into a Hiden Analytical HAL IV triple quadrupole mass spectrometer (QMS) for mass selection. Detection is achieved by a channeltron electron multiplier. Sensitivity is considerably enhanced by differential pumping which reduces the number of free electrons and secondary collisions in the QMS. Spectra recorded where the monochromator is scanned are flux normalised using a sodium salicylate (NaSal) window and visible photomultiplier tube (PMT) combination, which has a constant response over the energy range of the experiments. The apparatus and QMS, connected via a 1 mm diameter aperture, are pumped by separate turbo pumps which are backed by a common rotary pump, and the base pressure of the apparatus is approximately $10^{-7}$ mbar. With sample gas running, the typical pressure in the chamber is ca. $10^{-5}$ mbar. The pressure inside the chamber is measured using an ionisation gauge, the sensitivity of which to the sample under study is calibrated in a separate experiment relative to N$_2$ gas using a capacitance manometer (Table 1) [33,34].

Mass spectra are recorded to observe all the anions produced from photoabsorption of the sample gas by exposure to white light (i.e. using the monochromator set to zero order). The mass-to-charge ratio ($m/z$) of each peak in the mass spectrum is then fixed and the signal is recorded as a function of photon energy, typically over the range 8–35 eV. In addition, for each anion, its signal is recorded at a fixed photon energy (usually the energy of a peak observed in the spectrum) as a function of sample gas pressure over the typical range $(0.5–5.0) \times 10^{-5}$ mbar. As described in Section 1, anions which show a non-linear dependence with pressure cannot be assigned as ion-pair products, and their signal is most likely due to a two-step process such as dissociative electron attachment. Anions which show a linear dependence of signal with pressure can be attributed to ion-pair formation; being a unimolecular process, the rate of formation of ion pairs will then obey first-order kinetics.
Determination of absolute cross-sections and quantum yields for anion formation

Anion spectra resulting from ion-pair formation are presented as cross-sections, \( \sigma \), in absolute units of \( \text{cm}^2 \). The value of \( \sigma \) at a given photon energy \( h\nu \) is calculated by

\[
\sigma(h\nu) = k \left( \frac{SM}{frp} \right),
\]

where \( S \) is the detected signal in counts \( s^{-1} \), \( M \) is the relative mass sensitivity of the QMS, \( f \) is the relative photon flux (effectively a measure of the grating efficiency), \( r \) is the storage ring current, \( p \) is the sample gas pressure corrected for ionisation gauge sensitivity and \( k \) is a constant of proportionality. Correction to \( f \), \( r \) and \( p \) is straightforward, although this procedure cannot be used for anions produced by dissociative electron attachment because the anion signal is not a linear function of gas pressure. Correction to \( M \), however, is not trivial, and often seems to be ignored by others working in this field. An extensive set of experiments was therefore performed to determine \( M \) as a function of \( m/z \). All QMSs exhibit an element of mass discrimination, with a tendency to transmit heavier ions less efficiently [35]. To allow for this effect the mass factor, \( M \), has been determined by comparing the cation mass spectra of many polyatomic molecules in the QMS, following 70 eV electron impact ionisation, to ‘true’ mass spectra published in the electronic NIST database [36]. The values for \( M \) used in Equation (XII) are taken from the plot shown in Figure 3. It can be seen that as \( m/z \) increases, the detection efficiency of the QMS decreases and a higher value of \( M \) is required to allow for this effect.

The zero-blast effect is a phrase commonly used by mass spectrometrists. It arises because all ions entering the QMS may be transmitted when the lens potentials are set to detect \( m/z \) values close to zero [35]. This effect therefore becomes especially important when studying hydrogen-containing molecules since the tail of the zero-blast peak in the mass spectrum may overlap with \( m/z \) 1. Therefore, \( \text{H}^- \) spectra can only be trusted where there is no resemblance to other anion spectra recorded from the same molecule. Examples where this has caused severe problems include the weak \( \text{H}^- \) signal detected from \( \text{CH}_3Y \) molecules (\( Y = \text{F}, \text{Cl}, \text{Br} \)), which mimic the much stronger \( \text{Y}^- \) spectra [20].

### Table 1. Sensitivity factors, \( S \), for detection of the sample gases by the ion gauge detector used in the experiments relative to \( \text{N}_2 \) gas (\( S = 1 \)). The true gas pressure is given by the ion gauge reading/\( S \).

<table>
<thead>
<tr>
<th>Gas</th>
<th>( S )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 )</td>
<td>1.0</td>
</tr>
<tr>
<td>( \text{O}_2 )</td>
<td>0.95</td>
</tr>
<tr>
<td>( \text{SF}_6 )</td>
<td>2.7</td>
</tr>
<tr>
<td>( \text{CF}_4 )</td>
<td>1.7</td>
</tr>
<tr>
<td>( \text{C}_2\text{F}_6 )</td>
<td>3.2</td>
</tr>
<tr>
<td>( \text{CH}_4 )</td>
<td>1.7</td>
</tr>
<tr>
<td>( \text{CH}_3\text{Cl} )</td>
<td>3.5</td>
</tr>
<tr>
<td>( \text{CH}_3\text{F} )</td>
<td>1.65( ^a )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{Cl} )</td>
<td>3.0</td>
</tr>
<tr>
<td>( \text{CH}_3\text{F} )</td>
<td>3.0</td>
</tr>
<tr>
<td>( \text{CF}_2\text{Cl}_2 )</td>
<td>3.5</td>
</tr>
<tr>
<td>( \text{CF}_2\text{Cl}_2 )</td>
<td>1.6( ^a )</td>
</tr>
<tr>
<td>( \text{CF}_2\text{Cl}_2 )</td>
<td>3.7</td>
</tr>
<tr>
<td>( \text{CH}_3\text{F} )</td>
<td>3.7</td>
</tr>
<tr>
<td>( \text{CH}_3\text{Br} )</td>
<td>3.7</td>
</tr>
<tr>
<td>( \text{CH}_3\text{Cl} )</td>
<td>3.8</td>
</tr>
<tr>
<td>( \text{CH}_3\text{F} )</td>
<td>4.1( ^a )</td>
</tr>
<tr>
<td>( \text{CF}_3\text{F} )</td>
<td>1.65( ^a )</td>
</tr>
<tr>
<td>( \text{CF}_3\text{H} )</td>
<td>3.9( ^a )</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>2.3</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>3.7</td>
</tr>
<tr>
<td>( \text{CF}_3\text{H} )</td>
<td>2.6</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_6 )</td>
<td>2.6</td>
</tr>
<tr>
<td>( \text{C}_2\text{F}_6 )</td>
<td>2.9( ^a )</td>
</tr>
<tr>
<td>( \text{C}_2\text{F}_6 )</td>
<td>2.9( ^a )</td>
</tr>
<tr>
<td>( \text{SF}_6 )</td>
<td>3.6( ^a )</td>
</tr>
<tr>
<td>( \text{SF}_6 )</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Note: \( ^a \) Group additivity effects [33,34] are used to estimate these values, given in italics, where the data have not been measured.

4.1. Determination of absolute cross-sections and quantum yields for anion formation

Anion spectra resulting from ion-pair formation are presented as cross-sections, \( \sigma \), in absolute units of \( \text{cm}^2 \). The value of \( \sigma \) at a given photon energy \( h\nu \) is calculated by
(see Section 6.3). By contrast, H\(^-\) detected from CH\(_4\) is an example where this is not an issue because the H\(^-\) signal is dominant [19].

To determine absolute cross-sections, the signal corrected to \(f, r, p\) and \(M\) for F\(^-\) from SF\(_6\) is normalised to the known cross-section at 14.3 eV of \((7 \pm 2) \times 10^{-21}\) cm\(^2\) [9]. Likewise, the corrected signal for F\(^-\) from CF\(_4\) is normalised to its value at 13.9 eV of \((1.25 \pm 0.25) \times 10^{-21}\) cm\(^2\) [8]. It should be noted, however, that these cross-section values from Mitsuke \textit{et al.} are strictly not absolute, but are obtained from calibrated measurements of O\(^-\) yields from O\(_2\) [37]. Thus, normalisation factors \(k(\text{SF}_6)\) and \(k(\text{CF}_4)\) are determined. In theory, these two values should be the same. In practice, they vary by a factor ranging from 1.2 to 1.7. An average of the values is therefore used in

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**Figure 3 (colour online).** Graph to determine the relative mass sensitivity, \(M\), of the Hiden Analytical HAL IV QMS as a function of \(m/z\). Sample gases include CF\(_4\), SF\(_6\), SF\(_5\)CF\(_3\), CH\(_3\)F, CH\(_3\)Cl, CH\(_3\)Br, CH\(_2\)Cl\(_2\), CF\(_2\)Cl\(_2\), CFCl\(_3\), C\(_2\)H\(_4\), C\(_2\)H\(_6\), C\(_3\)H\(_8\), C\(_2\)F\(_4\), C\(_2\)F\(_6\), C\(_3\)F\(_8\), 2-C\(_4\)F\(_8\), c-C\(_4\)F\(_8\) and c-C\(_5\)F\(_8\), allowing ions of mass ranging from 12 to 212 u to be observed (solid squares). The mass spectrum of each sample was measured with 70 eV electron impact ionisation, and compared with the NIST spectrum [36]. At each \(m/z\) value, the % yield from NIST is divided by the % yield from the QMS spectrum, and the data are normalised to unity arbitrarily at \(m/z\) 69 (i.e. CF\(_3^+\)). The solid line shows the best fit to a third-order polynomial. Reprinted with permission from Ref [19]. Copyright 2010, Taylor and Francis.
Equation (XII) to determine cross-section values for anions from the sample under study. These measurements were made at every visit to the SRS, occurring typically every three months, and the appropriate value of \( k \) was used for each set of data collection. Overall, we believe that our values for anion cross-sections are accurate to an error no better than \( \pm 50–100\% \). Whilst this might seem disappointing, absolute measurements of this kind are notoriously difficult to make, and are prone to errors which have often, in our opinion, been underestimated in the literature.

At any photon energy, the quantum yield for anion production is determined by dividing the anion cross-section by the total photoabsorption cross-section at that energy. It represents the probability for anion formation, where this process is competing with other decay channels, such as neutral dissociation, molecular ionisation and fluorescence. In terms of unimolecular rate constants, \( k \), the quantum yield can be written as:

\[
\Phi_{\text{anion}} = \frac{k_{\text{anion}}}{\sum_i k_i} = \frac{k_{\text{anion}}}{k_{\text{anion}} + k_{\text{dissociation}} + k_{\text{ionisation}} + k_{\text{fluorescence}} + \cdots}.
\] (XIII)

Thus, total cross-section data from VUV photoabsorption spectroscopy are needed to determine \( \Phi_{\text{anion}} \). With the wide availability of tunable synchrotron radiation, whilst there has been a huge increase in the last 20 years in measurements of absorption cross-sections up to the lithium fluoride window edge of 11.8 eV (or 105 nm), often driven by the needs of atmospheric chemists [38], data for energies in the range 12–30 eV remain sparse except for the most stable of molecules such as CF\(_4\), SF\(_6\) and CH\(_4\). Furthermore, the Berkowitz review showed that anion formation is a very minor channel where other decay channels are energetically open, with quantum yields in the range ca. \( 10^{-7}\)–\( 10^{-2} \) [1]. A very high sensitivity of the apparatus is therefore necessary to observe the weak channels for anion production.

5. Results for SF\(_6\), CF\(_4\) and SF\(_5\)CF\(_3\)

The first molecule studied at Daresbury by negative photoion spectroscopy was the greenhouse gas trifluoromethyl sulphur pentafluoride, SF\(_5\)CF\(_3\), and full details are given in ref. [17]. The atmospheric significance of this work is described in Section 5.3. This molecule can be regarded either as a perturbed SF\(_6\) molecule in which one F atom is replaced by a CF\(_3\) radical, or a perturbed CF\(_4\) molecule in which one F is replaced by an SF\(_5\) radical. VUV absorption studies suggest the former is closer to the truth [39]. It therefore seemed sensible to study initially SF\(_6\) and CF\(_4\) by anion spectroscopy. With enhanced sensitivity in our experiment we were able to extend the earlier studies of Mitsuke et al. [8,9]. Thus the results presented here report a larger number of anions observed, Mitsuke et al. only observing formation of F\(^-\) from these two molecules. As explained in Section 4, these studies also allowed us to develop a method of calibration so that absolute cross-sections and quantum yields for anion production from unknown molecules could be determined.

5.1. SF\(_6\)

The white light negative ion mass spectrum for SF\(_6\) shows eight peaks corresponding to the anions F\(^-\) (100%), F\(_2\)\(^-\) (1%), SF\(_2\)\(^-\) (<1%), SF\(_2\)\(^-\) (<1%), SF\(_3\)\(^-\) (<1%), SF\(_4\)\(^-\) (<1%), SF\(_5\)\(^-\)
(2%) and SF$_6^-$ (67%). The relative signal strengths are shown in parentheses. Where sensitivity allowed, anion signals from SF$_6$ were recorded as a function of photon energy and are presented in Figure 4. Table 2 shows appearance energies of the anions, their cross-sections and quantum yields. For comparative purposes, Figure 4 includes the threshold photoelectron spectrum (TPES) of SF$_6$ [40]. Poor signal strengths prevented the ion yields of SF$_7^-$, SF$_8^-$, SF$_9^-$ and SF$_{10}^-$ from being recorded. SF$_6$ has $O_h$ symmetry, and the electronic configuration of the outer-valence molecular orbitals (MOs) can be written: $\ldots (1t_{1g})^6 (3e_g)^4 (1t_{2u})^6 (5t_{1u})^6 (1t_{1g})^6$. The F$^-$ and F$_2^-$ signals increase linearly with pressure, those of SF$_5^-$ and SF$_6^-$ non-linearly with the rate of change increasing as
pressure increases. Figure 5 shows the plot of anion signal versus SF\_6 pressure, with the behaviour of F\_− compared with SF\_5\_−. The linear pressure dependence of the F\_− and F\_2\_− anion signals suggest that they result from unimolecular ion-pair formation, whereas the SF\_5\_− and SF\_6\_− anions are formed by a secondary process. The cross-sections for F\_− and F\_2\_− can therefore be determined absolutely, whereas those for SF\_5\_− and SF\_6\_− cannot and only relative values are given.

The following ion-pair reactions are suggested as responsible for formation of F\_− and F\_2\_−:

\[
\text{SF}_6 \rightarrow \text{F}^- + \text{SF}_x^+ + (5 - x)\text{F} \quad (x \leq 5),
\]

\[
\text{SF}_6 \rightarrow \text{F}_2^- + \text{SF}_x^+ + (4 - x)\text{F} \quad (x \leq 4).
\]

The calculated enthalpy changes for reaction (5) are 10.4, 14.9, 15.5, 19.7 and 23.7 eV for \(x = 5, 4, 3, 2\) and 1, respectively. For reaction (6) they are 13.6, 14.1, 18.4 and 22.4 eV for \(x = 4, 3, 2\) and 1, respectively. F\_− produced from reaction (5) has been observed before.

### Table 2. Appearance energies, cross-sections and quantum yields for anions observed from photoexcitation of SF\_6, CF\_4, and SF\_3CF\_3.

<table>
<thead>
<tr>
<th>Molecule [AIE(^a) (eV)]</th>
<th>Anion</th>
<th>AE(^b) (eV)</th>
<th>Cross-section(^c) (cm(^2))</th>
<th>Energy(^d) (eV)</th>
<th>Quantum yield(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF_6 [15.1]</td>
<td>F_−</td>
<td>12.7</td>
<td>7.1 \times 10^{-21}</td>
<td>14.2</td>
<td>2.4 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>F_−</td>
<td>16.3</td>
<td>1.4 \times 10^{-22}</td>
<td>18.3</td>
<td>1.9 \times 10^{-6}</td>
</tr>
<tr>
<td></td>
<td>SF_5_−</td>
<td>15.1</td>
<td></td>
<td>17.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SF_6_−</td>
<td>15.1</td>
<td></td>
<td>17.1</td>
<td></td>
</tr>
<tr>
<td>CF_4 [15.4]</td>
<td>F_−</td>
<td>13.0</td>
<td>1.4 \times 10^{-21}</td>
<td>14.0</td>
<td>2.8 \times 10^{-5}</td>
</tr>
<tr>
<td></td>
<td>F_−</td>
<td>20.1</td>
<td>4.0 \times 10^{-23}</td>
<td>21.6</td>
<td>5.6 \times 10^{-7}</td>
</tr>
<tr>
<td>SF_3CF_3 [12.9]</td>
<td>F_−</td>
<td>11.05</td>
<td>3.4 \times 10^{-20}</td>
<td>16.9</td>
<td>3.4 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>F_−</td>
<td>16.1</td>
<td>1.2 \times 10^{-21}</td>
<td>17.9</td>
<td>1.1 \times 10^{-5}</td>
</tr>
<tr>
<td></td>
<td>SF_−</td>
<td>24.0</td>
<td>2.8 \times 10^{-22}</td>
<td>28.8</td>
<td>2.4 \times 10^{-6}</td>
</tr>
<tr>
<td></td>
<td>SF_2_−</td>
<td>20.2</td>
<td>3.9 \times 10^{-22}</td>
<td>24.2</td>
<td>2.5 \times 10^{-6}</td>
</tr>
<tr>
<td></td>
<td>SF_5_−</td>
<td>15.4</td>
<td>1.0 \times 10^{-20}</td>
<td>17.6</td>
<td>1.0 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>SF_6_−</td>
<td>13.0</td>
<td>1.3 \times 10^{-20}</td>
<td>14.1</td>
<td>1.7 \times 10^{-4}</td>
</tr>
<tr>
<td></td>
<td>SF_7_−</td>
<td>12.9</td>
<td></td>
<td>17.0</td>
<td></td>
</tr>
</tbody>
</table>

Notes: \(^a\)Adiabatic ionisation energy (AIE). Values are taken from the observed onset of ionisation for SF\_6 [40], CF\_4 [41] and SF\_3CF\_3 [42].

\(^b\)Appearance energy (AE) from this work. The error is estimated to be ±0.2 eV (except for F\_− from SF\_3CF\_3 for which the error is ±0.05 eV), based on the resolution and step size used to record ion yields.

\(^c\)Cross-section for anion production following photoexcitation of the parent molecule.

\(^d\)Energy of strongest peak. It is at this energy, where appropriate, where cross-section and quantum yield measurements are taken.

\(^e\)Quantum yields for anion production, obtained by dividing the anion cross-section (column 4) by the total photoabsorption cross-section. The latter values are given for SF\_6, CF\_4 and SF\_3CF\_3 in refs [43], [44], and [39], respectively.

\(^f\)Normalisation of the signal strength to determine an absolute cross-section is not possible because of the non-linear dependence of signal with pressure.

\(^g\)Quantum yield cannot be determined because the cross-section is not defined.
by Mitsuke et al. [9] in the photon energy range 11–31 eV and a detailed analysis was performed. Below 14.9 eV the associated cation can only be SF$_5^+$, and the present spectrum is in very good agreement with this earlier study. Scully et al. [45] have also observed the ion-pair products F$^-$ and F$_2^-$ from SF$_6$ in the higher photon energy range 20–205 eV, and both anions showed broad bands centred at 35.5 eV. Although not photoexciting SF$_6$ above 35 eV, our study clearly shows the onsets to these features. The F$_2^-$ spectrum in Figure 4 shows features in the energy range 16–21 eV not observed before. Below 18.4 eV it is not possible to say whether the associated cation is SF$_4^+$ or SF$_3^+$. The low F$_2^-$ cross-section is reflected in a poor signal-to-noise ratio. Three peaks are identified at 17.2, 18.2 and 19.7 eV. They most likely reflect the presence of Rydberg states which couple effectively to the ion-pair state, the peak energies therefore representing Rydberg transitions. Mitsuke et al. [9] found that the most prominent features in the F$^-$ ion yield at 13.2 and 14.3 eV were due to the ($1t_{1g})^{-1}4p$ and ($5t_{1u})^{-1}4s$ Rydberg transitions, respectively. The peaks in the F$_2^-$ ion yield at 17.2, 18.2 and 19.7 eV approximately match with peaks in the TPES of SF$_6$ at 17.1, 18.5 and 19.9 eV, respectively. A similar observation is made for the yield of F$_2^-$ from SF$_5$CF$_3$ (Section 5.3).

Figure 5 (colour online). Pressure dependence of F$^-$ and SF$_5^-$ anion signals from SF$_6$. A linear pressure dependence, shown by F$^-$, indicates the anion arises from a one-step, unimolecular ion-pair dissociation. A non-linear pressure dependence, shown by SF$_5^-$, suggests a more complicated, multi-step process is involved in formation of the anion. Reprinted with permission from Ref. [17]. Copyright 2008, American Institute of Physics.
Previous ion-pair experiments have also observed SF$_5^-$ and SF$_6^-$ from SF$_6$, their formation being attributed to the electron attachment process \[9,45\]:

\[ SF_6 + h\nu \rightarrow SF_6^+ + e^- , \]  
\[ SF_6 + e^- \rightarrow SF_6^- , \]  
\[ SF_6 + e^- \rightarrow SF_5^- + F. \]

SF$_6$ is a well-known electron scavenger, the rate coefficient at 300 K being $(2.38 \pm 0.15) \times 10^{-7}$ cm$^3$/s$^{-1}$ [46]. It attaches zero-energy electrons with a very large cross-section [47], and only reaction (8) can be responsible for the appearance of SF$_6^-$. Furthermore, Figure 4 highlights the striking similarities between the ion yield of SF$_6^-$ and the SF$_6$ TPES. This is a common effect for molecules with a very high rate coefficient for electron attachment, and is considered in more detail in Section 8.5.

### 5.2. CF$_4$

The white light negative ion mass spectrum for CF$_4$ shows three peaks corresponding to the anions F$^-$ (100%), CF$^-$ (1%) and F$_2^-$ (3%). The F$^-$ and F$_2^-$ signals were recorded as a function of photon energy and are shown in Figure 5, along with the TPES of CF$_4$ [41]. The corresponding data is shown in Table 2. The ion yield of CF$_4^+$ could not be measured due to poor signal strength. CF$_4$ has $T_d$ symmetry, and the electronic configuration of the outer-valence MOs can be written: ...(4a$_1$)$^2$ (3t$_2$)$^6$ (1e)$^4$ (4t$_2$)$^6$ (1t$_1$)$^6$.

The F$^-$ and F$_2^-$ signals both increase linearly with pressure, the cross-sections reported are therefore absolute values and the following ion-pair reactions are suggested for their formation:

\[ CF_4 \rightarrow F^- + CF_x^+ + (3 - x)F \quad (x \leq 3) , \]  
\[ CF_4 \rightarrow F_2^- + CF_x^+ + (2 - x)F \quad (x \leq 2) . \]

The calculated enthalpy changes for reaction (10) are 11.3, 17.7 and 20.7 eV for $x = 3, 2$ and 1, respectively; for (11) they are 16.3 and 19.3 eV for $x = 2$ and 1, respectively. The F$^-$ ion yield recorded here is in good agreement with the previous study of Mitsuke et al. [8] in the energy range 12–31 eV. The F$^-$ and F$_2^-$ yields are also in good agreement with those reported by Scully [34] at higher resolution in the photon range 20–35 eV (Figure 6c and d), but absolute cross-sections were not determined in their work. It is immediately obvious from Figure 6 that the F$^-$ and F$_2^-$ yields share a similar feature between 20 and 23 eV. Mitsuke et al. [8] assigned this feature in the F$^-$ yield to three Rydberg transitions $(3t_2)^{-1}np$ ($n = 4, 5$ or 6) at energies 20.96, 21.16 and 21.45 eV, respectively, converging on the third excited valence state of CF$_4^+$ ($\tilde{C}^2T_2$). The Rydberg states excited at these energies then couple to an ion-pair state which dissociates to F$^-$, the corresponding cation and any neutral fragments. The presence of Rydberg states in this energy region has also been observed in a high-resolution threshold photoelectron study of CF$_4$ by Yencha et al. [48]. Autoionising structure is observed from 20.3 to 21.6 eV, preceding the onset of the $\tilde{C}^2T_2$ state of CF$_4^+$ at 21.68 ± 0.01 eV [49]. This can be observed in the TPES in Figure 6 as a
slight rise above the baseline in the same energy range. It is therefore proposed that Rydberg states converging to CF$_4^+$ $\tilde{C}^2T_2$ couple to ion-pair states which dissociate to both F$^-$ and F$_2^-$. At 21.8 eV the F$^-$ cross-section is ca. 16 times larger than that of F$_2^-$. This may reflect the degree of coupling between states and/or the steric disadvantage of the formation of an extra bond to produce F$_2^-$. The feature between 20.0 and 23.5 eV in the F$^-$ ion yield has been recorded with better resolution, and is shown in Figure 7. It shows the CF$_4^+$ (3t$_2$)$^{-1}4p$, 5p and 6p overlapping Rydberg states converging on the CF$_4^+$ $\tilde{C}^2T_2$ state. Structure is also observed in the spectrum, showing the $v_4$(a$_1$) totally symmetric stretching mode in CF$_4^*$. These progressions have been observed before in the ion-pair study by Mitsuke et al. [8], and Table 3 compares the two sets of data, listing energy positions, energy spacings and the vibrational
quantum number assignments. The vibrational spacing of the progressions observed in these np Rydberg states in the F− ion yield average to 90 ± 5 meV. The assignments are taken directly from Mitsuke et al. Their quantum defect analysis yielded a δ value which is almost exactly the same for all three Rydberg states, ca. 0.60. This analysis also agrees with the photoabsorption study of Lee et al. [50]. Photoelectron spectroscopy shows a vibrational progression in the band representing ionisation to the $\tilde{C}^2T_2$ state of $\text{CF}_4^+$ with a spacing of ca. 90 meV and assigned to the $v_1$ C–F breathing mode [48], and a higher resolution optical emission spectrum of the $D^2A_1$$\rightarrow$$\tilde{C}^2T_2$ transition in $\text{CF}_4^+$ gave $v_1(\tilde{C}^2T_2) = 729 \pm 1 \text{ cm}^{-1}$ or 90.386 meV [51]. Since all these studies only involve excitation of the one totally symmetric vibrational mode in $T_d$ symmetry, the Jahn–Teller distortion in the triply degenerate $\tilde{C}^2T_2$ state of $\text{CF}_4^+$ is minimal.

Figure 7 shows an additional feature at 22.82 eV which was not observed in the previous studies. It is assigned to the (4a₁)$^{-1}3p$ Rydberg transition. This assignment uses a
value for the vertical ionisation energy of 25.11 eV for the fourth excited state of CF$_4^+$ with term symbol $\tilde{A}^2A_1$ [51]. The resulting term value of 2.29 leads to a quantum defect value of 0.56. This assignment is consistent with the observation of features in the F$^-$ ion yield at 24.00 and 24.45 eV by Mitsuke et al. [8], and assigned by them to the $(4a_1)^{-1}4p$ and $(4a_1)^{-1}5p$ Rydberg transitions, the next two members of this $p$ Rydberg series, with $\delta$ values of 0.50 and 0.46, respectively [8]. The next discrete state in the photoelectron
spectrum, corresponding to ionisation of the 2t_2 inner-valence electron, is the \( \tilde{E}^2T_2 \) state at 40.3 eV [52]. Both the F^- and F_2^- yields increase above 25 eV, and the spectral features at higher energies are more clearly observed in the work of Scully [34] which extends to 110 eV.

5.3. \( \text{SF}_3\text{CF}_3 \)

It is important to put the work to be reported into an atmospheric context. The presence of \( \text{SF}_3\text{CF}_3 \) in the atmosphere was first reported 11 years ago by Sturges et al. [53]. Although the atmospheric concentrations of \( \text{SF}_3\text{CF}_3 \) are still very low, its lifetime is very long, ca. 800–1000 years [44], it has the highest molecular radiative forcing of anthropogenic greenhouse gases through absorption of infrared radiation in the wavelength range of 5–30 \( \mu \)m and has a global warming potential 18,000 times greater than that of \( \text{CO}_2 \) [54]. Since its discovery, \( \text{SF}_3\text{CF}_3 \) has been the focus of numerous studies aimed to better understand its spectroscopic properties and reactivity, and also its atmospheric sources and sinks. Of anthropogenic origin, \( \text{SF}_3\text{CF}_3 \) has been linked to \( \text{SF}_6 \) production and the manufacture of fluorochemicals [53], but the main source of this potent greenhouse gas has not yet unambiguously been identified. Having no hydrogen atoms, \( \text{SF}_3\text{CF}_3 \) is not oxidised via reaction with the \( \text{OH} \) radical in the troposphere, and UV photolysis in the stratosphere is unlikely to contribute significantly to a sink mechanism due to the absence of photoabsorption by \( \text{SF}_3\text{CF}_3 \) below 8 eV [44,55] and the high value of the \( \text{SF}_5^-\text{CF}_3 \) bond dissociation energy, 3.86 ± 0.45 eV [56].

The microscopic physical and chemical processes that remove \( \text{SF}_3\text{CF}_3 \) from the atmosphere therefore occur at higher altitude in the mesosphere. One process could be ion-pair formation following VUV absorption due to the high intensity of this radiation, especially Lyman-\( \alpha \) radiation at 10.2 eV that exists in this region of the atmosphere [44]. Other processes include ion–molecule reactions and electron attachment. Ion–molecule reaction studies have shown that both cations and anions react rapidly with \( \text{SF}_3\text{CF}_3 \) [58,59], and may therefore remove it from the upper atmosphere. However, the concentration of atmospherically relevant ions (e.g. \( \text{O}^+, \text{O}_3^+, \text{N}^+, \text{N}_2^+ \)) is so low that the pseudo-first-order rate constant for ion–molecule reactions, \( \Sigma k_{\text{ion}[\text{ion}] \text{ion}} \), is too small for this channel to contribute to any significant extent [56]. Low-energy electron attachment to \( \text{SF}_3\text{CF}_3 \) is relatively fast, \( 7.7 \times 10^{-8} \) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) at 298 K [60], and the absorption cross-section at the Lyman-\( \alpha \) wavelength of 121.6 nm is surprisingly high, \( 1.3 \times 10^{-19} \) cm\(^2\) [39,44,55]. With certain assumptions, we showed that the electron attachment process is responsible for ca. 99% of the removal of \( \text{SF}_3\text{CF}_3 \) in the mesosphere, VUV photodissociation is responsible for the remaining ca. 1% [44,56]. One of the possible products which is energetically allowed following VUV photoexcitation of \( \text{SF}_3\text{CF}_3 \) at 121.6 nm is ion-pair formation to \( \text{CF}_3^+ + \text{SF}_5^- \). It was for this rationale that we performed a complete negative photoion spectroscopic study of \( \text{SF}_3\text{CF}_3 \) over the full range of the vacuum-UV, and absolute cross-sections and quantum yields were evaluated for all anions observed [17]. These results are described below. However, the long lifetime of \( \text{SF}_3\text{CF}_3 \) in the earth’s atmosphere, 800–1000 years, ultimately is not determined by such microscopic chemical processes that occur in the mesosphere, but by much slower macroscopic meteorology that transports the pollutant from the earth’s surface up into the mesosphere [44,56].
The white light negative ion mass spectrum for SF₅CF₃ shows eight peaks corresponding to the anions F⁻ (100%), CF⁻ (1%), F₂⁻ (2%), SF⁻ (1%), SF₂⁻ (1%), SF₃⁻ (1%), SF₄⁻ (2%) and SF₅⁻ (14%). With the exception of SF₅⁻, all anion signals show a linear dependence with the pressure of SF₅CF₃. SF₅⁻ shows a similar pressure behaviour to its formation from SF₆, discussed in Section 5.1. Absolute cross-sections and quantum yields for the anions resulting from ion-pair formation are presented in Figure 8, the data in Table 2. The quantum yields all fall in the range 10⁻⁶–10⁻⁴, consistent with expectations for a large polyatomic molecule [1,24]. The ion yield of F⁻ below 12 eV was recorded with a LiF window in the beamline, transmitting only \( h\nu < 11.8 \) eV, to display the threshold.

Figure 8 (colour online). Cross-sections for anion production following photoexcitation of SF₅CF₃. Ion yields were recorded as a function of photon energy between 10.5 and 35.0 eV with a step size of 0.1 eV and a wavelength resolution of 0.6 nm. Solid red arrows in spectra (a)–(f) show enthalpy values of the thermochemical thresholds calculated for reactions (12)–(17), respectively. Reprinted with permission from Ref. [17]. Copyright 2008, American Institute of Physics.
region more clearly. An appearance energy ($ AE_{298} $) value of $ 11.05 \pm 0.05 \text{ eV} $ was determined.

The following reactions are suggested as the main sources for six of the anions:

$$ \text{SF}_5\text{CF}_3 \rightarrow \text{F}^- + \text{CF}_3^+ + \text{SF}_4, \quad (12) $$

$$ \text{SF}_5\text{CF}_3 \rightarrow \text{SF}_3^- + \text{CF}_3^+ + \text{F} + \text{F}, \quad (14) $$

$$ \text{SF}_5\text{CF}_3 \rightarrow \text{F}_2^- + \text{CF}_3^+ + \text{SF}_3, \quad (15) $$

$$ \text{SF}_5\text{CF}_3 \rightarrow \text{SF}_2^- + \text{CF}_3^+ + 3\text{F}, \quad (16) $$

$$ \text{SF}_5\text{CF}_3 \rightarrow \text{SF}^- + \text{CF}_3^+ + 4\text{F}. \quad (17) $$

In all cases the cation formed is $ \text{CF}_3^+ $, the associated anion therefore resulting from the $ \text{SF}_5 $ part of the $ \text{SF}_5\text{CF}_3 $ molecule. An alternative mechanism to reaction (12) for production of $ \text{F}^- $ might be from dissociative electron attachment, e.g.

$$ \text{SF}_5\text{CF}_3 + \text{e}^- \rightarrow \text{F}^- + \text{SF}_4 + \text{CF}_3. \quad (18) $$

This possibility is rejected because the only product of low-energy electron attachment to $ \text{SF}_5\text{CF}_3 $ is $ \text{SF}_5^- $ (reaction (20)) [60], and we note the much stronger signal of $ \text{F}^- $ compared to that of $ \text{SF}_5^- $ (Figures 8 and 9).

The $ \text{S}–\text{C} $ bond is most likely to be the weakest in the molecule, the dissociation energy at 0 K measured to be $ 3.86 \pm 0.45 \text{ eV} $ [56]. In addition, Xu et al. [57] have calculated bond dissociation energies at 298 K in $ \text{SF}_5\text{CF}_3 $, resulting in $ D^0_{298} (\text{SF}_5\text{CF}_2–\text{F}) > D^0_{298} (\text{F}–\text{SF}_4\text{CF}_3) > D^0_{298} (\text{SF}_5^-\text{CF}_3) $. One cannot say conclusively that reactions (12)–(17) are responsible for all of the signal from these six anions across the complete energy range studied. Certainly, more channels become energetically accessible at higher energies. It is, however, interesting that the thermochemical thresholds for reactions (12)–(17), 11.5, 13.4, 16.0, 14.3, 20.0 and 23.0 eV respectively, approximately reflect the observed AE values for the corresponding anion (Table 2). The only exception is reaction (15), production of $ \text{F}_2^- $, where steric constraints on forming a new $ \text{F}–\text{F} $ bond could be responsible. This trend can be visualised in Figure 8 by vertical arrows representing the enthalpies of the calculated thermochemical thresholds. No errors are given, but there is significant uncertainty in some of the $ \Delta H^\circ_{298} $ values used which probably explains why the calculated AE value is sometimes greater than the experimental value (e.g. $ \text{F}^- $ and $ \text{SF}_4^- $ in Figure 8). The formation of $ \text{F}^- $ and $ \text{F}_2^- $ over the complete energy range 11–35 eV is unlikely to result exclusively from reactions (12) and (15), respectively, whereas the channels available to form the sulphur-containing anions are fewer. Indeed, the ion yields of $ \text{F}^- $ and $ \text{F}_2^- $ do show structure over a much wider energy range than those of $ \text{SF}_5^- (x = 1–4) $.

The ion yields for $ \text{F}^- $, $ \text{F}_2^- $ and $ \text{SF}_5^- $ are presented in Figure 9 and compared to the TPES of $ \text{SF}_5\text{CF}_3 $ [42]. $ \text{SF}_5^- $ is the only anion detected which is not associated with ion-pair formation, and therefore only its relative yield can be determined. Three comparisons can be made between the behaviour of $ \text{SF}_5^- $ formed from $ \text{SF}_5\text{CF}_3 $ and $ \text{SF}_5^- $ formed from $ \text{SF}_6 $.
First, for both molecules the SF$_5^-$ signal increases non-linearly with pressure, with the rate of change of signal increasing as the pressure increases. Second, electron attachment to SF$_5$CF$_3$ is dissociative, forming SF$_5^-$ + CF$_3$ as the only significant channel [60]. Third, the yield of SF$_5^-$ from SF$_5$CF$_3$ shows many similarities to the TPES of SF$_5$CF$_3$. The dominant mechanism for the production of SF$_5^-$ from SF$_5$CF$_3$ is likely, therefore, to be dissociative electron attachment following photoionisation of the parent molecule as the source of low-energy electrons:

$$\text{SF}_5\text{CF}_3 + h\nu \rightarrow \text{SF}_5\text{CF}_3^+ + e^-,$$

(19)

$$\text{SF}_5\text{CF}_3 + e^- \rightarrow \text{SF}_5^-(\text{CF}_3).$$

(20)

As shown in Figure 9, the F$^-$ and F$_2^-$ ion yields also show similarities to the TPES of SF$_5$CF$_3$. Due to its higher signal-to-noise ratio, it is the F$^-$ spectrum where these similarities are most obvious. In the photon energy range 13–23 eV the agreement between peak positions is good and the relative signal strengths show only small differences.
The resemblance of the F$^{-}$ ion yield to the TPES could be explained by a process involving electron attachment being significant in F$^{-}$ formation. However, the F$^{-}$ signal rises linearly with increasing gas pressure, suggesting strongly that a primary process, i.e. ion-pair formation to F$^{-}$ + SF$_4$CF$_3$ (or F$^{-}$ + CF$_4^+$ + SF$_4$), is dominant. The features in the F$^{-}$ yield are labelled 1–11 in Figure 8. The experimental AE$_{298}$ (F$^{-}$) is 11.05 ± 0.05 eV, and this anion gives rise to peak 1 centred at 11.7 eV. This peak occurs below the onset of ionisation for SF$_2$CF$_3$, 12.9 eV [42], so the presence of photoelectrons from reaction (19) is not relevant. The energy of peak 1 is close to peaks observed in the SF$_2$CF$_3$ photoabsorption and total fluorescence yield spectra at 11.4 eV [39,61]. These two studies give different assignments to this transition. Holland et al. [39] assign it to a blend of several valence–valence transitions, whilst Ruiz et al. [61] assign it to the (29a$'$)$^{-1}$s Rydberg transition, where 29a$'$ is the highest occupied MO. Following dissociation of SF$_2$CF$_3$, fluorescence at this energy was reported to originate from the CF$_3$ fragment. In addition, this was the most intense band observed within the photon energy range studied of 10–28 eV [61]. It must represent a transition to the same intermediate state which predissociates along two different reaction coordinates to yield CF$_3^+$ and F$^{-}$ anions. The ion-pair quantum yield at this maximum in the F$^{-}$ ion yield at 11.7 eV is $\Phi = 1.5 \times 10^{-4}$. This small value, coupled with the fact that fluorescence from SF$_2$CF$_3$ is unlikely to have a large quantum yield, strongly suggests that predissociation into neutral fragments is the favoured process at this energy, not ion-pair formation. The agreement of peak positions in SF$_2$CF$_3$ between the photoabsorption spectrum, the total fluorescence yield and the F$^{-}$ ion yield extends up to 17 eV. Above this energy, similarities between the spectra are less clear.

It is interesting that the F$^{-}$ ion-pair quantum yield does not decrease above the onset of ionisation of SF$_2$CF$_3$ at 12.9 eV. Features 1 and 4 at 11.7 and 16.9 eV, for example, have $\Phi = 1.5 \times 10^{-4}$ and $3.4 \times 10^{-4}$, respectively (Table 4). As a result of significant photoabsorption leading to ionisation, one would expect the ion-pair quantum yield to decrease, as observed for both SF$_6$ and CF$_4$ (Table 4). However, the opposite occurs for SF$_2$CF$_3$. In fact, features 2–11 of Figure 8 occur at, or just below, vertical ionisation energies in the TPES of SF$_2$CF$_3$ [42]. Only feature 1 does not follow this trend. It seems unlikely that valence states of SF$_2$CF$_3$ which predissociate into ion pairs coincidentally lie very close to the ionisation thresholds, certainly across this large energy range. It is much more likely that Rydberg states play an important role. Certainly the F$^{-}$ ion yield could be explained if coupling to ion-pair states was more significant from Rydberg states close to the ionisation thresholds than from those lower in energy. Contributions to the F$^{-}$ ion yield from low-lying Rydberg states would then be the dominant cause of peak 1, and very likely a weak background across the spectrum. F$^{-}$ ions produced via high-lying Rydberg states would be dominant at higher energy, and hence responsible for features 2–11 in the ion yield. If this is true, it negates the generally accepted rule that it is low-$n$, and not high-$n$, Rydberg states which interact most strongly with ion-pair states. However, most of the ion-pair experiments on polyatomics to date have studied halogenated molecules where the lowest ion-pair threshold lies below the first ionisation energy [1], so by definition it is the low-$n$ states which have been the most widely studied.

This analysis also extends to the yields of SF$_4^-$, SF$_3^-$, F$_2^-$, SF$_2^-$ and SF$_-$; their peak positions and observed structure can be explained in the same way as for F$^{-}$. The SF$_4^-$, SF$_3^-$ and SF$_2^-$ yields show less structure than is seen from F$^{-}$. In the energy regions where
peaks are observed, their energies agree with those in the F− ion yield, and hence with vertical ionisation energies of SF5CF3. It is likely that the number of available ion-pair states reflects the structure seen in the ion yields. SF4−, for example, is likely to arise from reaction (13) only. It is certainly the channel that is most sterically unhindered. Coupling of high-lying Rydberg states to this ion-pair state will give rise to the peaks in the SF4− yield at 14.0 and 15.0 eV (Figure 8). The absence of structure above 16 eV represents the energy where this ion-pair state no longer couples significantly to Rydberg states. SF3− and SF2− may also arise through coupling of high-lying Rydberg states to an appropriate ion-pair state, and only over a limited energy range above onset. By contrast, many more dissociation channels will be available to yield the F− and F−2 anions. As a result, extensive structure in both ion yields extends from onset to 25 eV. Finally, we observe that shape resonances have been observed in the yields of many anions in both SF6 and CF4 above 25 eV [45,34]. There is no obvious evidence for such peaks in the anion yields from SF5CF3, but it would be surprising if they were not present.

The difficulties in assigning peaks in the total fluorescence yield spectrum of SF5CF3 have already been noted by Ruiz et al. [61], and at our modest resolution there are several Rydberg transitions which could be assigned to peaks 2–11 in Figure 8(a). Indeed, there is even disagreement whether transitions observed in the VUV absorption spectrum of SF5CF3 and the CF3+ fluorescence excitation spectrum are due to valence or Rydberg transitions. Peaks in the absorption and electron energy loss spectra of SF5CF3 have been assigned by Limao-Vieira et al. [62] to Rydberg transitions, and quantum defects determined. Ruiz et al. [61] also assign peaks in the absorption spectrum leading to CF3+ fluorescence to Rydberg transitions. Holland et al. [39], however, assign the main peaks in the absorption spectrum to valence transitions. The spectra presented here observe a different exit channel, i.e. photodissociation of excited states of SF5CF3 leading to production of anions. However, the primary excitation process in all these experiments is the same, and their assignment to Rydberg transitions is favoured for two reasons. First, all previous work on ion-pair production from polyatomic molecules has preferred the process of Rydberg state photoexcitation, followed by predissociation into an ion-pair state [1,16]. Second, apart from the low-energy peak in the F− yield at 11.7 eV below the ionisation energy of SF5CF3−, all F− peaks have energies very close to peaks in the TPES of this molecule. Since it is Rydberg states that have energies converging on ground and excited electronic states of SF5CF3+, it seems very likely that these F− peaks correspond to photoexcitation of Rydberg states.
The dominant VUV radiation in the mesosphere is Lyman-\(\alpha\) radiation with a photon wavelength of 121.59 nm or energy of 10.20 eV. If production of anion(s) or ion-pair dissociation are important sink routes for SF\(_5\)CF\(_3\) in the mesosphere, it is the processes occurring at this energy that will be the most important. Ion-pair dissociation of SF\(_5\)CF\(_3\) to both CF\(_3^-\) + SF\(_5^+\) and SF\(_5^-\) + CF\(_3^+\) are energetically open channels at this energy, these two reactions having small \(\Delta_r H_{298}^\circ\) values of only +1.82 and −0.90 eV, respectively [44]. The enthalpy of reaction to produce F\(^-\) + SF\(_4\)CF\(_3^+\) is not known due to the enthalpy of formation of SF\(_4\)CF\(_3^+\) being unknown. However, since anion formation appears to occur indirectly in SF\(_5\)CF\(_3\) via initial excitation of Rydberg states, no anions can be observed until the lowest Rydberg states are accessed. The VUV absorption spectrum shows that this does not happen until energies exceed 8 eV [39,44,55], the appearance energies of F\(^-\) and SF\(_5^-\) are 11.05 ± 0.05 and 12.9 ± 0.2 eV (see earlier), and CF\(_3^-\) is not observed. No anions are observed at 10.20 eV. Thus it appears that anion or ion-pair formation does not contribute to the processes removing SF\(_5\)CF\(_3\) from the earth’s atmosphere in the mesosphere, and the only two significant microscopic processes are dissociative electron attachment and photodissociation at 10.20 eV to neutral species [44,56].

6. Results for SF\(_5\)Cl, CF\(_3\)X (X = Cl, Br, I) and CH\(_3\)Y (Y = F, Cl, Br)

One obvious question to ask about the formation of anions from a polyatomic molecule is whether the anions which are formed from a non-symmetrical molecule and their cross-sections bear any relation to the strength of the breaking bond. In both SF\(_5\) and CF\(_4\), all the six and four bonds in the parent molecule, respectively, have equal strength. However, if the symmetry of either molecule is reduced by replacing one fluorine by a chlorine atom, for example, one may ask whether F\(^-\) or Cl\(^-\) are more likely to form following VUV photoexcitation, and whether their appearance energies relate in any way to the relative strength of the S(C)–F and S(C)–Cl bonds. In polyatomic cations of this size, e.g. CF\(_2\)H\(_2^+\), when two different bonds can break, assuming the ground state of the cation is bound for at least some of its vibrational levels, the first fragment cation is that produced by cleavage of the weakest bond. The second cation is formed by cleavage of the second-weakest bond, etc. Thus, in unpublished work from the high-resolution VUV beamline of the Swiss Light Source, using imaging photoelectron photoion coincidence spectroscopy we have measured the AE\(_{0K}\) of CF\(_2\)H\(_2^+\) from CF\(_2\)H\(_2\) to be 13.060 ± 0.002 eV, whilst the AE\(_{0K}\) of CFH\(_2^+\) is ca. 1 eV higher at 14.00 ± 0.03 eV [63]. These data correlate with bond strengths in the neutral molecule, with \(D_{298}^e(\text{H–CHF}_2)\), 4.48 ± 0.04 eV, being weaker than \(D_{298}^e(\text{F–CH}_2\text{F})\), 5.14 ± 0.09 eV [64]. The same ordering is maintained in the cationic species, with \(D_{298}^e(\text{H–CHF}_2^+)\), \(\leq 0.1 \pm 0.1\) eV, now being much weaker than \(D_{298}^e(\text{F–CH}_2\text{F}^+)\), \(\leq 2.5 \pm 0.1\) eV (Table 11) [22]. These upper limits for \(D_{298}^e(\text{A–BC}^+)\) were obtained from Equation (III) using experimental values for the appearance energies of H\(^-\) and F\(^-\) following VUV photoexcitation of CF\(_2\)H\(_2\). This forms the rationale to study molecules related to SF\(_6\) and CF\(_4\), e.g. SF\(_5\)Cl and CF\(_3\)X (X = Cl, Br, I) in which one fluorine atom is replaced by a different halogen atom, by anion spectroscopy [21,18]. We then investigate whether the presence of fluorine atoms is significant by studying the CH\(_3\)Y (Y = F, Cl, Br) series [20]. This section summarises the results.
6.1. $\text{SF}_5\text{Cl}$

The structure of SF$_5$Cl, $C_{4v}$ symmetry in the gas phase, has been established by microwave spectroscopy and electron diffraction [65,66]. Four equatorial S–F bonds have a slightly shorter length, 0.157 nm, than the S–F axial bond, 0.159 nm, whilst that of S–Cl is significantly longer, 0.204 nm. The relative ordering of the valence MOs of the molecule has been calculated using self-consistent discrete variational $X\alpha$ methods [67], and there have been two photoelectron studies by He I/He II and threshold electron spectroscopy [68,69]. The fragmentation dynamics of the electronic states of SF$_5$Cl$^+$ has been studied by threshold photoelectron photoion coincidence spectroscopy [69]. Chim et al. [69] also reported results from a Gaussian 03 calculation [70] which supported the MO assignments made by Klyagina et al. [67]. Figure 10 summarises the combined findings of these

![Figure 10 (colour online). Valence MOs assigned to energy maxima of features (indicated by solid lines with numeric values, in eV) observed in experimental photoelectron spectra for SF$_6$ [40,41] and SF$_5$Cl [68,69], and the correlation between the orbitals. Orbitals in parenthesis are thought to lie close in energy but have not yet been resolved in experimental spectra. Reprinted with permission from Ref. [21]. Copyright 2010, American Chemical Society.](image-url)
investigations, and correlates the MOs for SF₅Cl with those of SF₆ of O₉ symmetry. The studies of anion formation following excitation of SF₅Cl are even more limited. There have been two measurements of the thermal electron attachment rate coefficient to SF₅Cl: $(4.8 \pm 1.2) \times 10^{-8}$ cm$^3$ s$^{-1}$ by van Doren et al. [71] and $(2.0 \pm 0.3) \times 10^{-8}$ cm$^3$ s$^{-1}$ by Mayhew et al. [46], a factor of ca. 5–12 slower than the value for SF₆, $(2.38 \pm 0.15) \times 10^{-8}$ cm$^3$ s$^{-1}$. Under thermal electron conditions, electron attachment to SF₅Cl is dissociative, producing SF$_5^-$(92%), Cl$^-$ (5%) and FCl$^-$ (3%), whereas that to SF$_6$ is predominantly non-dissociative. A recent crossed beam study of SF$_5$Cl with low-energy electrons in the range 0–14 eV [72] has clarified inconsistencies arising from an earlier study [73]. As in the thermal experiment, electron attachment to SF$_5$Cl is dissociative with SF$_5^-$ being the dominant anion at low electron energies, but resonances forming F$^-$, Cl$^-$ and FCl$^-$ are now observed at $E > 3$ eV.

Only three anions, F$^-$, Cl$^-$ and SF$_5^-$ were detected following VUV photoexcitation of SF$_5$Cl in the photon energy range 10–25 eV. The F$^-$ signal was by far the strongest, followed by Cl$^-$ whilst SF$_5^-$ was detected only just above the sensitivity limit of the apparatus. The signals of F$^-$ and Cl$^-$ show a linear dependence with pressure, showing that these ions form by an ion-pair process. As with SF$_6$ and SF$_5$CF$_3$, the SF$_5^-$ signal from SF$_5$Cl shows a non-linear dependence with pressure, with the signal rising more rapidly with pressure than from a linear relationship. As before, this suggests that SF$_5^-$ most likely results from the two-step process of dissociative electron attachment: SF$_5$Cl + hν → SF$_5$Cl$^+$ + e$^-$, followed by SF$_5$Cl$^+$ + e$^-$ → SF$_5^-$ + Cl, where a quadratic dependence of SF$_5^-$ signal with pressure is predicted. It is noted immediately that the strength of the F$^-$ signal is somewhat surprising, given that the F–SF$_4$Cl bond dissociation energy, 3.70 eV, is significantly stronger than that of Cl–SF$_5$, 2.54 eV [69].

The cross-section for F$^-$ formation is shown in Figure 11(a) over the range 12–30 eV. Its onset is 12.7 ± 0.2 eV (Figure 11(b)) which lies above the adiabatic ionisation energy (AIE) for SF$_5$Cl of 12.3 eV. The onset is gradual, with an enhanced gradient for $h \nu >$ ca. 13.6 eV (labelled shoulder ‘1’ in Figure 11(b)). The maximum cross-section, 6.1 × 10$^{-20}$ cm$^2$, occurs at an energy of 14.06 eV, labelled ‘2’ in the figure. The shoulder between 12.7 and 13.6 eV may arise from

$$\text{SF}_5\text{Cl} \rightarrow \text{F}^- + \text{SF}_4\text{Cl}^+ \quad \Delta_r H_{298}^0 \leq 11.58 \text{ eV}, \quad (21)$$

$$\text{SF}_5\text{Cl} \rightarrow \text{F}^- + \text{SF}_3^+ + \text{FCl} \quad \Delta_r H_{298}^0 = 11.41 \text{ eV}, \quad (22)$$

$$\text{SF}_5\text{Cl} \rightarrow \text{F}^- + \text{SF}_3\text{Cl}^+ + \text{F} \quad \Delta_r H_{298}^0 \text{ unknown.} \quad (23)$$

SF$_3$Cl$^+$ has not been observed in any photon or electron-induced dissociative ionisation experiment, suggesting that production of F$^-$ from reaction (23) is unlikely. The increase in gradient of the $\sigma$ versus $h \nu$ spectrum at 13.6 eV may correlate with production of F$^-$ from

$$\text{SF}_5\text{Cl} \rightarrow \text{F}^- + \text{SF}_4^+ + \text{Cl} \quad \Delta_r H_{298}^0 = 13.47 \text{ eV}. \quad (24)$$

At higher energies it becomes even more difficult to assign features in ion-pair spectra to specific dissociation reactions with any confidence because with the lower symmetry of the
molecule compared to SF$_6$, the number of accessible ion-pair products increases dramatically, e.g.

$$\text{SF}_5\text{Cl} \rightarrow \text{F}^- + \text{Cl}^+ + \text{SF}_3 + \text{F} \quad \Delta_c H_{298}^o = 18.64 \text{ eV}$$ (25)

Feature 1 of the F$^-$ ion yield exhibits the characteristics associated with direct ion-pair formation; a gradual onset and a broad structureless spectrum. Features 2–9 show the characteristics associated with indirect formation (see Section 2), and have been assigned.

Figure 11 (colour online). Cross-section for F$^-$ formation from SF$_5$Cl. (a) Spectrum from 12 to 30 eV recorded with a step size of 0.05 eV and a wavelength resolution of 0.6 nm. (b) Spectrum from 12.5 to 15.0 eV recorded with a step size of 0.005 eV and a wavelength resolution of 0.12 nm. (c) An expansion of (a) between 15 and 26 eV. All of the observable features in the F$^-$ cross-section are labelled 1–8 in spectra (b) and (c), see Section 6.1. Reprinted with permission from Ref. [21]. Copyright 2010, American Chemical Society.
to Rydberg states of SF$_5$Cl (Table 5). These data assume that, in most cases, the given Rydberg state converges towards the excited state of SF$_5$Cl$^+$ closest in energy to that of the resonance. For example, it is assumed that feature 2 at 14.06 eV converges to SF$_5$Cl$^+$ $^2A_1$ at 14.79 eV, and not to SF$_5$Cl$^+$ $^2B_2$ at 15.35 eV. These higher energy peaks, 3–9, are much weaker with cross-sections approximately one order of magnitude weaker than the cross-section of peak 2; thus the cross-section at 23.2 eV, corresponding to feature 6, is only $5.9/10^{21}$ 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 $^2A_1$ state of SF$_5$Cl$^+$ involves the removal of an electron from the 15$a_1$ MO which has both S–Feq and S–Cl bonding character [70]; the Rydberg state represented by feature 2 is thought to converge to the first excited state of SF$_5$Cl$^+$, and has been identified to come from reaction (24) where an S–F bond and an S–Cl bond in the molecule are both broken. Of course, it is not known whether the F$^{-}$ signal comes from one of the four equivalent equatorial S–F bonds, or from the longer and weaker axial S–F bond.

The ion yield of Cl$^{-}$ is shown in Figure 12, only one peak at 10.9 eV was detected in the range 8–35 eV, and its onset is $10.6 \pm 0.2$ eV. This energy lies below the ionisation energy of SF$_5$Cl, and therefore Cl$^{-}$ can only be formed from an ion-pair reaction. The only energetically allowed reaction is

$$\text{SF}_5\text{Cl} \rightarrow \text{Cl}^- + \text{SF}_5^+ \quad \Delta_e H_{298} = 8.72 \text{ eV}$$ (26)

with the onset occurring 1.9 eV above the thermochemical threshold. The sharp onset implies that this ion-pair product forms indirectly. This feature can be assigned to a resonant transition from the highest occupied MO of SF$_5$Cl to the 4$p$ Rydberg state converging on SF$_5$Cl$^+$ $^2E$ which then predissociates into the Cl$^{-} +$ SF$_5^+$ ion-pair state.

### Table 5. Rydberg assignments to features observed in the F$^-$ ion yield recorded following the photoexcitation of SF$_5$Cl, recorded with a step size of 0.05 eV and a wavelength resolution of 0.6 nm.

<table>
<thead>
<tr>
<th>Feature$^a$</th>
<th>E (eV)$^b$</th>
<th>IE$^c$</th>
<th>$\delta^d$</th>
<th>Assignment$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>14.06</td>
<td>14.79 ($^2A_1$)</td>
<td>1.68</td>
<td>(15$a_1$)$^{-1}$ 6p</td>
</tr>
<tr>
<td>3</td>
<td>16.80</td>
<td>18.07 ($^2A_1$)</td>
<td>1.73</td>
<td>(14$a_1$)$^{-1}$ 5p</td>
</tr>
<tr>
<td>4</td>
<td>20.65</td>
<td>21.0 ($^2A_1$)</td>
<td>1.80</td>
<td>(13$a_1$)$^{-1}$ 8p</td>
</tr>
<tr>
<td>5</td>
<td>21.65</td>
<td>21.9 ($^2E$)</td>
<td>1.70</td>
<td>(5e)$^{-1}$ 5p</td>
</tr>
<tr>
<td>6</td>
<td>23.20</td>
<td>25.1 ($^2A_1$)</td>
<td>1.33</td>
<td>(12$a_1$)$^{-1}$ 4p</td>
</tr>
<tr>
<td>7</td>
<td>23.95</td>
<td>25.1 ($^2A_1$)</td>
<td>1.56</td>
<td>(12$a_1$)$^{-1}$ 5p</td>
</tr>
<tr>
<td>8</td>
<td>24.60</td>
<td>25.1 ($^2A_1$)</td>
<td>1.78</td>
<td>(12$a_1$)$^{-1}$ 7p</td>
</tr>
</tbody>
</table>

Notes: $^a$Feature in the F$^-$ ion yield as labelled in Figure 11.

$^b$Photon energy of the feature (Figure 11). The uncertainty in these values is estimated to be $\pm 0.01$ eV for feature 2, $\pm 0.1$ eV for features 3–8.

$^c$The electronic state of SF$_5$Cl$^+$ to which the assigned Rydberg state converges. Values of the vertical ionisation energy are taken from DeKock et al. [68].

$^d$Value of the quantum defect calculated from the Rydberg formula, Equation (V).

$^e$Rydberg orbital assignment. The numbering scheme for the MOs of SF$_5$Cl (Figure 10) is that used by Klyagina et al. [67] and Parkes [70], where both core and valence orbitals are counted.
with data for high-lying Rydberg states (Table 5). The Cl\(^{-}\) ion yield in Figure 12 could not be put accurately onto an absolute scale because the signal level was so 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 \cite{18,20}, it is estimated that the maximum cross-section for Cl\(^{-}\) production is less than ca. 10\(^{-22}\) cm\(^2\). From Equation (II) an upper limit for the S–F and S–Cl bond dissociation energy in SF\(_5\)Cl at 298 K can be determined. Using AE(F\(^{-}\)) = 12.7 ± 0.2 eV, an upper limit for \(D_{298}^0(\text{F–SF}_4\text{Cl})\) of 4.8 ± 0.3 eV is obtained. Likewise, using AE(Cl\(^{-}\)) = 10.6 ± 0.2 eV, an upper limit for \(D_{298}^0(\text{Cl–SF}_5)\) of 4.4 ± 0.3 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 SF\(_5\)Cl \cite{69}.

The apparent absence of ion-pair reactions producing Cl\(^{-}\) with any significant yield is not easily explained. The quantum yield for production of either F\(^{-}\) or Cl\(^{-}\) cannot be quantified because absolute VUV absorption cross-sections in the range 10–20 eV are not known for SF\(_5\)Cl. However, the yield of F\(^{-}\) is orders of magnitude higher, despite the S–F bond being ca. 50% stronger than the S–Cl bond. Furthermore, the thermochemical energy of the lowest channel producing F\(^{-}\), i.e. F\(^{-}\) + SF\(_4\)Cl\(^{+}\), is ca. 2.8 eV higher than that for production of Cl\(^{-}\), i.e. Cl\(^{-}\) + SF\(_5\)\(^{+}\). It would appear that the dynamics of the crossing of Rydberg states with the ion-pair continuum determines the relative intensities of the two atomic anions that can be formed, and not the thermochemistry of the different

Figure 12 (colour online). The observation of Cl\(^{-}\) anions following photoexcitation of SF\(_5\)Cl in the range 8–15 eV. The spectrum was recorded with a step size of 0.1 eV and a wavelength resolution of 0.6 nm. The spectrum could not be put onto an absolute scale, but the maximum the cross-section is probably less than ca. 10\(^{-22}\) cm\(^2\). Reprinted with permission from Ref. [21]. Copyright 2010, American Chemical Society.
dissociation channels or the physical properties (e.g. electron affinity, electronegativity or polarisability) of the corresponding neutral atom.

6.2. CF3X (X = Cl, Br, I)

A similar situation is observed with the CF3X series of molecules [18], in which one F atom in the symmetrical CF4 molecule is replaced by a different halogen atom; competition can occur between cleavage of the C–F and the C–X bond. In addition to F− and X− anions being observed, a large range of other anions are also observed: F2−, FX−, CF−, CF2−, and CF3−. With the exception of Br− and I−, all the observed anions show a linear dependence of signal with pressure. The dissociative electron attachment process dominates the production of Br− and I−. Unlike SF5Cl, all cross-sections for anions produced by ion-pair formation can be put on to an absolute scale by calibrating the signal strengths with those of F− from both SF6 and CF4 (Section 4.1). Furthermore, since data for VUV absorption cross-sections are available [74–76], quantum yields can be determined. The data are shown in Table 6, with Figures 13 and 14 showing the F− and X− ion yields from CF3X, respectively. (These figures also show, where available, the absorption, threshold photoelectron and fluorescence excitation spectra of these molecules, showing that the Br− and I− spectra from CF3Br and CF3I show some similarity with the threshold photoelectron spectra which is not present in the four other anion yields.) Absolute cross-sections are reported for F− from CF3X and Cl− from CF3Cl, but clearly not for Br− and I− from CF3Br and CF3I. However, there is one exception. The lowest energy peak in the I− yield at 9.0 eV, with a threshold of 8.8 ± 0.2 eV, occurs at an energy below the AIE of CF3I, 10.4 eV [78]. It can therefore only arise from ion-pair formation, e.g.

\[
\text{CF3I} \rightarrow \text{I}^- + \text{CF}_3^+ \quad \Delta_r H^o_{298} = 8.3 \text{ eV.} \tag{27}
\]

For this one peak, we can determine the cross-section for I− formation to be \(3.8 \times 10^{-21} \text{cm}^2\) and, via normalisation to the absorption cross-section, a quantum yield of ca. \(8 \times 10^{-5}\).

The F− signal from CF3X shows an onset at 16.0 ± 0.2, 14.7 ± 0.2 and 9.7 ± 0.2 eV for X = Cl, Br and I, respectively. On thermochemical grounds, it seems likely that the F− anion from CF3X (X = Cl and Br) arises in combination, not with CF2X+ (28), but with CF2+ + X, since the enthalpies of reactions (28)–(29) are close to these values,

\[
\text{CF3Cl} \rightarrow \text{F}^- + \text{CF}_2^+ + \text{Cl} \quad \Delta_r H^o_{298} = 15.8 \text{ eV}, \tag{28}
\]

\[
\text{CF3Br} \rightarrow \text{F}^- + \text{CF}_2^+ + \text{Br} \quad \Delta_r H^o_{298} = 14.9 \text{ eV.} \tag{29}
\]

The energy of the equivalent channel in CF3I is 14.2 eV, yet signal is observed at lower energy (Figure 13c). We can predict with confidence that the weak peak in the F− yield from CF3I at 9.8 eV can only arise from F− forming with CF2I+, even though the enthalpy of formation of CF2I+ is unknown. The energies of the equivalent channels for CF3Cl and CF3Br are 10.2 and ≤10.1 eV, so it seems unlikely that F− above ca. 15 eV from these molecules forms from this channel.
For CF$_3$Cl, the quantum yield for production of F$^-$ at the energy of the first maximum at 21 eV, $1.8 \times 10^{-4}$, exceeds that for production of Cl$^-$ at the same energy by a factor of ca. 6. This comparison cannot be made for CF$_3$Br and CF$_3$I. In the former case, Br$^-$ only forms by dissociative electron attachment. In the latter case, the absorption cross-section for CF$_3$I at 20.4 eV has not been measured. Whilst the data are not as conclusive as that

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Anion</th>
<th>AE$^b$ (eV)</th>
<th>Cross-section maximum$^c$ (cm$^2$)</th>
<th>Energy$^d$ (eV)</th>
<th>Quantum yield$^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$Cl [12.4]</td>
<td>F$^-$</td>
<td>16.0</td>
<td>$1.5 \times 10^{-20}$</td>
<td>21.0</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Cl$^-$</td>
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<td>$2.3 \times 10^{-21}$</td>
<td>20.9</td>
<td>$2.9 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>F$_2^-$</td>
<td>ca. 21$^f$</td>
<td>$6.8 \times 10^{-23}$</td>
<td>22.7</td>
<td>$8.5 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>FCl$^-$</td>
<td>ca. 18$^f$</td>
<td>$6.5 \times 10^{-23}$</td>
<td>20.8</td>
<td>$8.0 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>CF$^-$</td>
<td>25.5$^g$</td>
<td>$1.6 \times 10^{-22}$</td>
<td>27.3</td>
<td>$2.0 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>CF$_2^-$</td>
<td>20.2</td>
<td>$1.5 \times 10^{-22}$</td>
<td>21.3</td>
<td>$1.8 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>CF$_3^-$</td>
<td>15.5</td>
<td>$2.8 \times 10^{-22}$</td>
<td>18.1</td>
<td>$3.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>CF$_3$Br [11.5]</td>
<td>F$^-$</td>
<td>14.7</td>
<td>$9.7 \times 10^{-21}$</td>
<td>19.6</td>
<td>$1.2 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>Br$^-$</td>
<td>15.1</td>
<td>$--$</td>
<td>$--$</td>
<td>$--$</td>
</tr>
<tr>
<td></td>
<td>F$_2^-$</td>
<td>ca. 19$^f$</td>
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<td>20.4</td>
<td>$3.4 \times 10^{-6}$</td>
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<td>CF$^-$</td>
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<td>$3.4 \times 10^{-22}$</td>
<td>25.6</td>
<td>$5.2 \times 10^{-6}$</td>
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<td>CF$_2^-$</td>
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<td>19.5</td>
<td>$5.8 \times 10^{-6}$</td>
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<td></td>
<td>CF$_3^-$</td>
<td>13.6</td>
<td>$2.5 \times 10^{-22}$</td>
<td>14.8</td>
<td>$4.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>CF$_3$I [10.4]</td>
<td>F$^-$</td>
<td>9.7</td>
<td>$1.1 \times 10^{-20}$</td>
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<tr>
<td></td>
<td>I$^-$</td>
<td>8.8</td>
<td>$--$</td>
<td>$--$</td>
<td>$--$</td>
</tr>
<tr>
<td></td>
<td>F$_2^-$</td>
<td>ca. 17$^f$</td>
<td>$8.5 \times 10^{-23}$</td>
<td>20.1</td>
<td>$--$</td>
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<td></td>
<td>CF$^-$</td>
<td>21.6</td>
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<tr>
<td></td>
<td>CF$_2^-$</td>
<td>16.0</td>
<td>$4.6 \times 10^{-22}$</td>
<td>16.8</td>
<td>$--$</td>
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<tr>
<td></td>
<td>CF$_3^-$</td>
<td>11.0</td>
<td>$5.7 \times 10^{-22}$</td>
<td>12.7</td>
<td>$--$</td>
</tr>
</tbody>
</table>

Notes: 

$^a$Adiabatic ionisation energy (AIE) for CF$_3$Cl [77], CF$_3$Br [77] and CF$_3$I [78].

$^b$Appearance energy (AE) from this work. The error is estimated to be ±0.2 eV, based on the resolution and step size used to record the ion yields.

$^c$Cross-section for anion production following photoexcitation of the parent molecule.

$^d$Energy of peak maximum at which cross-section and quantum yield measurements are taken.

$^e$Quantum yields for anion production, obtained by dividing cross-sections for anions (column 4) by total photoabsorption cross-sections. The latter values are given for CF$_3$Cl and CF$_3$Br [74,75].

$^f$Cannot state AE with any confidence due to poor signal/noise.

$^g$There is some ambiguity surrounding the mass of anions detected contributing to the CF$^-$ ion yield from CF$_3$Cl. The signal observed in the range 16–25 eV is thought to arise from Cl$^-$ ions, and the value of 25.5 eV represents our interpretation of the true onset of CF$^-$ anions.

$^h$Quantum yield is not calculated because photoabsorption cross-section for CF$_3$Cl is not available at this energy.

$^i$The Br$^-$ and I$^-$ ion yields are significantly influenced by anions arising from dissociative electron attachment. Cross-sections, and hence quantum yields, cannot therefore be determined. The one exception is I$^-$ at 9.0 for which we estimate a cross-section of $3.8 \times 10^{-21}$ cm$^2$ and a quantum yield of $8 \times 10^{-5}$ (see Section 6.2).

$^j$Quantum yields cannot be calculated, because photoabsorption data for CF$_3$I are limited to photon energies <12 eV.
for SF$_5$Cl (Section 6.1), the conclusion from this study of formation of F$^-$ and X$^-$ from CF$_3$X is that the F$^-$ anion probably forms with a higher quantum yield than X$^-$, even though the C–F bond is significantly stronger than the C–X bond. The data for these molecules are complicated by the multiple possibilities of the cation (+ neutral) that are

![Figure 13](colour online). Cross-sections for F$^-$ production following photoexcitation of (a) CF$_3$Cl, and (b) CF$_3$Br between 12 and 32 eV. The total photoabsorption spectra [75], threshold photoelectron spectra [77] and total fluorescence yields [75] for CF$_3$Cl and CF$_3$Br are included for comparative purposes. (c) Cross-section for F$^-$ production following photoexcitation of CF$_3$I between 8 and 32 eV. The TPES [80] and total fluorescence yield [75] are included. All F$^-$ ion yields were recorded with a step size of 0.1 eV and a wavelength resolution of 0.6 nm. This resolution is equivalent to ca. 0.2 eV at 20 eV. Reprinted with permission from Ref. [18]. Copyright 2009, American Institute of Physics.
Figure 14 (colour online). (a) Cross-section for Cl\(^-\) production following photoexcitation of CF\(_3\)Cl in the energy range 12–34 eV. The total photoabsorption spectrum [75], TPES [77] and total fluorescence yield [75] for CF\(_3\)Cl are included for comparative purposes. The Cl\(^-\) ion yield was recorded with a step size of 0.1 eV and a wavelength resolution of 0.6 nm. (b) Cross-section for Br\(^-\) production following photoexcitation of CF\(_3\)Br between 12 and 28 eV, with the TPES superimposed on top [77]. (c) I\(^-\) ion yield recorded following photoexcitation of CF\(_3\)I between 8 and 28 eV, with the 8–12 eV range expanded by a factor of 30. The TPES [80] is superimposed on top of the I\(^-\) ion yield. The anion spectra cannot be put onto an absolute scale because the signals are shown to change non-linearly with pressure. The peak at 9.0 eV in the I\(^-\) spectrum, however, can only result from ion-pair formation and the cross-section at this energy is 3.8 \(\times\) 10\(^{-21}\) cm\(^2\). Reprinted with permission from Ref. [18]. Copyright 2009, American Institute of Physics.
formed with the anion, and by the presence of dissociative electron attachment in CF$_3$Br and CF$_3$I being dominant. But the trend that these molecules prefer to form F$/\text{CO}$ rather than X$/\text{CO}$ following VUV excitation seems clear. The shape of the peaks in the anion ion yield spectra suggest that these anions form via an indirect process. As with SF$_5$Cl, if this is true it can only mean that the dynamics of the crossing of the initially excited Rydberg state of CF$_3$X with the ion-pair continuum is the dominant process in determining the relative quantum yields of the atomic anions that are formed.

Data from ion-pair formation of F$/\text{CO}$ from SF$_6$, SF$_5$Cl and SF$_5$CF$_3$ are collected in Table 7. Two points are striking. First, the relative energy of the AE(F$/\text{CO}$) to the AIE of the parent molecule may be important. The most significant features in the F$/\text{CO}$ spectrum from SF$_6$ appear below its AIE [9,17], yet for SF$_5$Cl the AE(F$/\text{CO}$) and the first F$/\text{CO}$ peak exceed the AIE [21]. The same comment can be made when comparing F$/\text{CO}$ from CF$_4$ with F$/\text{CO}$ from CF$_5$Cl [8,17,18,79]; for CF$_4$ the AE(F$/\text{CO}$) is less than the adiabatic IE, whereas for CF$_5$Cl the AE(F$/\text{CO}$) exceeds the adiabatic IE. 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 autoionisation process. It is possible, therefore, that the change in symmetry on substituting a fluorine for a chlorine atom suppresses the formation of ion pairs below the ionisation energy, or possibly increases the probability of a competing process such as neutral dissociation (e.g. SF$_5$Cl$^* \rightarrow$ SF$_5$ + Cl). We note that when comparing data for ion-pair formation from CF$_5$Cl with photoabsorption and fluorescence excitation spectra [75], the evidence suggests that photoexcitation below the ionisation energy almost exclusively results in neutral photodissociation. Second, production of F$/\text{CO}$ from the molecules of lower symmetry appears to be accompanied by a simultaneous bond cleavage to form an anion plus neutral species. For example, SF$_5$Cl probably forms F$/\text{CO}$ + SF$_4^+$ + Cl and not F$/\text{CO}$ + SF$_4$Cl$^+$, CF$_3$Cl forms F$/\text{CO}$ + CF$_2^+$ + Cl and not F$/\text{CO}$ + CF$_2$Cl$^+$, SF$_5$CF$_3$ forms F$/\text{CO}$ + CF$_3^+$ + SF$_4$ and not F$/\text{CO}$ + SF$_4$CF$_3^+$. From SF$_6$ and CF$_4$, however, F$/\text{CO}$ appears to form at threshold with SF$_2^+$ (and not with SF$_4^+$ + F) and CF$_3^+$ (and not CF$_2^+$ + F), respectively. If this is a generic effect, the reason for it is unclear.

Table 7. Comparison of data obtained for ion-pair formation of F$/\text{CO}$ from SF$_6$, SF$_5$Cl and SF$_5$CF$_3$. A separate comparison for CF$_4$ and CF$_3$Cl is also included.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>AIE$^a$ (eV)</th>
<th>AE(F$/\text{CO}$)$^b$ (eV)</th>
<th>Reaction at AE$^c$</th>
<th>E$(\sigma_{\text{max}})^d$ (eV)</th>
<th>Reaction at $\sigma_{\text{max}}^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF$_6$</td>
<td>15.1</td>
<td>12.7 ± 0.2</td>
<td>SF$_6$ → F$/\text{CO}$ + SF$_4^+$</td>
<td>14.2</td>
<td>SF$_6$ → F$/\text{CO}$ + SF$_2^+$</td>
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<tr>
<td>SF$_5$Cl</td>
<td>12.3</td>
<td>12.7 ± 0.2</td>
<td>Not known</td>
<td>14.06</td>
<td>SF$_5$Cl → F$/\text{CO}$ + SF$_4^+$ + Cl</td>
</tr>
<tr>
<td>SF$_5$CF$_3$</td>
<td>12.9</td>
<td>11.05 ± 0.05</td>
<td>SF$_5$CF$_3$ → F$/\text{CO}$ + CF$_3^+$ + SF$_4$</td>
<td>16.9</td>
<td>Not known</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>15.4</td>
<td>13.0 ± 0.2</td>
<td>CF$_4$ → F$/\text{CO}$ + CF$_3^+$</td>
<td>14.0</td>
<td>CF$_4$ → F$/\text{CO}$ + CF$_3^+$</td>
</tr>
<tr>
<td>CF$_3$Cl</td>
<td>12.4</td>
<td>16.0 ± 0.2</td>
<td>CF$_3$Cl → F$/\text{CO}$ + CF$_2^+$ + Cl</td>
<td>21.0</td>
<td>Not known</td>
</tr>
</tbody>
</table>

Notes: $^a$AIE for SF$_6$ [40], SF$_5$Cl [68,69], SF$_5$CF$_3$ [42], CF$_3$Cl [77] and CF$_4$ [48].

$^b$Appearance energy of F$/\text{CO}$ anions, this work.

$^c$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$/\text{CO}$.

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6.3. CH$_3$Y (Y = F, Cl, Br)

The common theme from Sections 6.1 and 6.2 is that F$^-$ forms with the highest cross-section from substituted SF$_6$ and CF$_4$ molecules when one F atom is replaced by a larger halogen atom X, even though the S(C)–F bond is significantly stronger than the S(C)–X bond. It seems unlikely, but the five- and three-fold statistical weighting in favour of production of F$^-$ from SF$_5$Cl and CF$_3$X, respectively, may be one important factor. To investigate this effect further, we have studied the CH$_3$Y (Y = F, Cl and Br) series of molecules [20] to see if H$^-$ is the dominant anion. For this series of molecules, the bond strength should not be an issue because the H–CH$_2$Y bond strength is less than, comparable to, or exceeds that of the Y–CH$_3$ bond; the former have values of 4.39, 4.34 and 4.43, the latter have values of 4.77, 3.63 and 3.05 eV for Y = F, Cl and Br, respectively [64]. We did not study CH$_3$I because previous work has shown that the cross-sections of any anions are too small to produce measurable quantities of ion pairs in the VUV region [1].

Our work reported the observation of Y$^-$, H$^-$, CHY$^-$ and CH$_2$Y$^-$, significantly extending the work of Suzuki et al. [10] in which only the Y$^-$ anion was reported. Unlike the situation with CF$_3$X (Section 6.2), the signal of all these anions shows a linear dependence with pressure, showing that they all arise from ion-pair formation and not from dissociative electron attachment. Unfortunately, the question posed in the previous paragraph cannot be easily addressed quantitatively because it is difficult to determine absolute cross-sections for H$^-$ formation from these CH$_3$Y molecules because this anion is not dominant. The H$^-$ ion yields are therefore perturbed by the zero-blast effect (Section 4.1) [35]. However, the most significant experimental observation is that the dominant anion from all three molecules is production of Y$^-$, and the ion yields for production of F$^-$ from CH$_3$F, Cl$^-$ from CH$_3$Cl and Br$^-$ from CH$_3$Br in the range 10–30 eV are shown in Figures 15(a), 16(a) and 17(b), respectively. Absolute cross-sections and quantum yields (Table 8) are determined in the normal way. H$^-$ is observed from all three molecules, but for CH$_3$F and CH$_3$Cl the spectrum mimics that of F$^-$ and Cl$^-$, respectively; the normalised H$^-$ signal is ca. 10 and 40 times weaker than that of F$^-$ or Cl$^-$ from CH$_3$F or CH$_3$Cl, respectively. Only for CH$_3$Br with photon energies in excess of 12 eV, ca. 2.5 eV above threshold for production of Br$^-$, was the H$^-$ spectrum significantly different from the Br$^-$ spectrum. It was then possible to perform a subtraction procedure, and extract the true H$^-$ ion yield over the energy range of 12–30 eV (Figure 17(a)), although it was not possible to trust with confidence the absolute cross-section values that were obtained. The important result is that production of the halogen anion dominates that of H$^-$. Furthermore, this fact seems independent of the molecule and the relative strengths of the C–Y and C–H bonds, and the three-fold statistical weighting favouring production of H$^-$. Further information on the energetics and mechanism of Y$^-$ formation from CH$_3$Y can be obtained from higher resolution studies of the threshold region. Figure 18 shows the three threshold regions recorded with a resolution of ca. 0.02 eV. Onsets for Y$^-$ formation at 298 K are determined to be 12.28 ± 0.02, 10.04 ± 0.02 and 9.46 ± 0.02 eV for Y = F, Cl and Br, respectively. These values lie below the respective ionisation energies to the $X^2E_3/2$ state of CH$_3$Y$^+$ of 12.53, 11.29 and 10.54 eV [85,86], but exceed the respective thermochemical values for the appearance energy, given by $D^0_{298}(Y$–CH$_3$) + IE(CH$_3$) – EA(Y), of 11.21, 9.85 and 9.52 eV for X = F, Cl and Br. The inequality of Equation (II) is therefore obeyed in all three cases. Unlike the CF$_3$X series (Section 6.2),
Figure 15 (colour online). Absolute cross-sections for F\(^{-}\), CF\(^{-}\), CHF\(^{-}\) and CH\(_2\)F\(^{-}\) production following vacuum-UV photoexcitation of CH\(_3\)F. Ion yields were measured between 12 and 32 eV at a wavelength resolution of 0.6 nm. Solid arrows show the energies of the thermochemical thresholds calculated for all possible dissociation reactions. The relevant channels to the text are (1) corresponding to the formation of F\(^{-}\) + CH\(_3^+\), (7) to the formation of CHF\(^{-}\) + H\(^+\) + H and (8) to the formation of CH\(_2\)F\(^{-}\) + H\(^+\). Reproduced with permission from Ref. [20].

Figure 16 (colour online). Absolute cross-sections for Cl\(^{-}\) and CH\(_2\)Cl\(^{-}\) production following vacuum-UV photoexcitation of CH\(_3\)Cl. Ion yields were measured between 8 and 34 eV at a wavelength resolution of 0.6 nm. Solid arrows (9) and (12) show the energies of the thermochemical thresholds calculated for formation of Cl\(^{-}\) + CH\(_3^+\) and CH\(_2\)Cl\(^{-}\) + H\(^+\), respectively. Reproduced with permission from Ref. [20].
energetically it is only possible for $Y^-$ to form with $\text{CH}_3^+$ at threshold, and further fragmentation to $\text{CH}_2^+ + \text{H}$ is endothermic in all three molecules, e.g.

$$\text{CH}_3\text{F} \to \text{F}^- + \text{CH}_3^+ \quad \Delta_r H_{298}^\circ = 11.18 \text{ eV},$$  

but

$$\text{CH}_3\text{F} \to \text{F}^- + \text{CH}_2^+ + \text{H} \quad \Delta_r H_{298}^\circ = 16.47 \text{ eV}.$$

Perhaps most revealing with respect to the mechanism for ion-pair formation, the $\text{F}^-$ ion yield shows no structure whereas discrete transitions can be identified in the $\text{Cl}^-$ and $\text{Br}^-$ yields. The latter yields are indicative of indirect ion-pair formation in which Rydberg states of $\text{CH}_3\text{Cl}$ and $\text{CH}_3\text{Br}$ are populated, followed by predissociation into the $\text{Cl}^-(\text{Br}^-) + \text{CH}_3^+$ ion-pair continuum. There are two strong pieces of evidence to support this. First, the ground-state photoelectron band of both $\text{CH}_3\text{Cl}$ and $\text{CH}_3\text{Br}$ has only limited vibrational structure, with the strongest transitions occurring to $v^+ = 0$ [85,86]. Thus Rydberg transitions in $\text{CH}_3\text{Cl}$ and $\text{CH}_3\text{Br}$ converging on the $\tilde{X}^2E$ state of the parent ion would not be expected to exhibit extensive vibrational progressions, and the structure in Figure 18(b) and (c) can only be Rydberg in nature. Second, there is an exact similarity of the $\text{CH}_3^+$ ion yield from photoionisation mass spectrometric studies to these $Y^-$ ion yields [86,87]; this is as expected, since $Y^- + \text{CH}_3^+$ is the only ion-pair channel that is energetically open. It is noted, however, that earlier photoabsorption studies by the same group of Locht et al. at a resolution of ca. 0.01 eV suggest that there is generally good, but not perfect agreement between the absorption spectrum and the $\text{Cl}^-(\text{Br}^-)$ ion yield spectrum below the ionisation energy of $\text{CH}_3\text{Cl}$ and $\text{CH}_3\text{Br}$ [82,83]. This suggests that competing
dissociation channels, such as neutral photodissociation, are operative with a finite quantum yield. By contrast, the ground-state photoelectron band of CH3F has extended vibrational structure [85]. The origin of the F⁻/C0 signal from CH3F is more uncertain, as its first maximum just exceeds the AIE, and thus cannot correspond to Rydberg states converging on $\nu^+ = 0$ of CH3F⁺ $\tilde{X}^2E$. Given the large width of the peak and its lack of structure, it is most likely that it corresponds to a direct ion-pair transition. Alternatively, Suzuki et al. [10] have suggested that this peak consists of unresolved Rydberg states converging to a number of vibrationally excited levels of CH3F⁺ $\tilde{X}^2E$.

The Y⁻/C0 signal from CH3Y also shows discrete structure at higher energies above 15 eV (Figure 19). The broad, vibrationally unresolved bands are assigned to Rydberg states converging on the $\tilde{C}^2A_1$ state of CH3Y⁺, and partially resolved vibrational structure is observed in the (2a1)⁻14s Rydberg state of CH3Cl which mimics structure in the absorption spectrum [88]. The onsets of the Cl⁻ and Br⁻ signals around 15 eV suggest that these ions are now forming with a cation that has resulted from fragmentation of CH3⁺, i.e.

\[
\text{CH}_3\text{Cl} \rightarrow \text{Cl}^- + \text{CH}_2^+ + \text{H} \quad \Delta_r H_{298}^o = 15.14 \text{ eV}, \quad (32)
\]

\[
\text{CH}_3\text{Br} \rightarrow \text{Br}^- + \text{CH}_2^+ + \text{H} \quad \Delta_r H_{298}^o = 14.77 \text{ eV}. \quad (33)
\]
Figure 18 (colour online). The threshold region for production of Y\(^-\) from CH\(_3\)Y recorded with a step size of 0.005 eV and a wavelength resolution of 0.2 nm, corresponding to ca. 0.02 eV at 12 eV. Absolute cross-sections are not shown because the calibration signals of F\(^-\) from CF\(_4\) and SF\(_6\) were not measured at this resolution: (i) and (ii) show the energies of the adiabatic and vertical ionisation energy of the first photoelectron band of CH\(_3\)F [85], (iii) shows the energy of the AIE of the first band of CH\(_3\)Cl, ionisation to CH\(_3\)Cl\(^+\) X\(^2\)E where the spin-orbit splitting is very small, 0.027 eV [85] and (iv) and (v) show the energies of the AIE of the two spin-orbit components of CH\(_3\)Br\(^+\) X\(^2\)E\(_{3/2}\) and \(^2\)E\(_{1/2}\) where the spin-orbit splitting is much larger, 0.320 eV [86]. Reproduced with permission from Ref. [20]. Copyright 2010, Royal Society of Chemistry.

Figure 19 (colour online). Relative cross-sections for production of Y\(^-\) from CH\(_3\)Y between 14 and 28 eV recorded at a resolution of 0.6 nm. The arrows show the vertical ionisation energies of the fourth photoelectron band, ionisation to C\(^2\)A\(_1\). A progression with approximate spacing of 0.27 eV is observed in feature 3 of the Cl\(^-\)/CH\(_3\)Cl spectrum, probably corresponding to vibrational structure in the (2a\(_1\))\(^{-1}\)4s Rydberg state of CH\(_3\)Cl [88]. Reproduced with permission from Ref. [20]. Copyright 2010, Royal Society of Chemistry.
This onset for $F^-$ from $\text{CH}_3\text{F}$ at 18.5 eV suggests that the equivalent reaction is probably also operative,

$$\text{CH}_3\text{F} \rightarrow F^- + \text{CH}_2^+ + \text{H} \quad \Delta_r H_{298}^o = 16.47 \text{ eV}. \quad (34)$$

However, it is energetically possible that the highest energy band, marked F3, in the three spectra of Figure 19 may correspond to dissociation to $\text{Y}^- + \text{CH}_3^+ + 2\text{H}$. In addition to formation of $\text{Y}^-$ with $\text{CH}_3^+$, cleavage of the C–Y bond following VUV excitation can also result in the formation of the ion pair $\text{CH}_3^- + \text{Y}^+$. Yet $\text{CH}_3^+$ is not observed from any of the three molecules. Whatever the dynamics of ion-pair formation, these channels are forbidden by energetics, except possibly for the highest energy bands from $\text{CH}_3\text{Cl}$ and $\text{CH}_3\text{Br}$, i.e.

$$\text{CH}_3\text{F} \rightarrow \text{CH}_3^- + \text{F}^+ \quad \Delta_r H_{298}^o = 22.15 \text{ eV}, \quad (35)$$

$$\text{CH}_3\text{Cl} \rightarrow \text{CH}_3^- + \text{Cl}^+ \quad \Delta_r H_{298}^o = 16.53 \text{ eV}, \quad (36)$$

$$\text{CH}_3\text{Br} \rightarrow \text{CH}_3^- + \text{Br}^+ \quad \Delta_r H_{298}^o = 14.76 \text{ eV}. \quad (37)$$

Cleavage of the C–H bond can likewise result in two ion pairs, $\text{H}^- + \text{CH}_2\text{Y}^+$ and $\text{CH}_2\text{Y}^- + \text{H}^+$. $\text{CH}_2\text{Y}^-$ is observed from all three molecules, and absolute cross-sections and quantum yields are shown in Figures 15–17 and in Table 8. Comparison to the yields of $\text{H}^-$ is not possible due to the difficulties associated with quantifying the $\text{H}^-$ signals due to the zero-blast effect.

### 6.4. Conclusions from ion-pair formation in non-symmetric molecules

The main conclusion from the work on non-symmetric molecules described in Sections 6.1–6.3 is that halogen atoms preferentially form their atomic anion following VUV excitation into Rydberg states of halogen-containing polyatomic molecules, and this dominates production of $\text{H}^-$ or polyatomic fragment anions. Where two halogen anion channels are possible it appears that one anion is nearly always dominant. So, for example, $\text{F}^-$, and not $\text{Cl}^-$, preferentially forms from $\text{SF}_5\text{Cl}$ and $\text{CF}_3\text{Cl}$. It is not clear whether this is due to the smaller mass, the smaller size or the greater electronegativity of one anion versus another. It does appear, however, that the dynamics of the crossing of the Rydberg state with the ion-pair continuum appears to be the dominant process that determines which anion is formed preferentially. Unfortunately, calculations of potential energy curves in this region of photon excitation, 10–20 eV, are very scarce even for molecules of high symmetry such as $\text{SF}_6$, $\text{CF}_4$ and $\text{CH}_4$. All other factors, such as the thermochemistry of the different exit channels and the microscopic properties of the different anions (such as size, electron affinity, electronegativity or polarisability of the neutral atom) seem to be second-order effects.

### 7. Bond dissociation energies from ion-pair induced photochemistry

Using the inequality of Equation (II), the experimental AE values for anion formation at 298 K determined in this work from $\text{CF}_3\text{X}$ and $\text{CH}_3\text{Y}$ can be used to calculate an upper
limit to the bond dissociation energy, $D_{298}^\circ$, when the AE value correlates with single-bond breaking ion-pair formation. When the unimolecular dissociation involves multiple bond-breaking or the formation of a new bond, calculations performed in this way become over-complicated and too many assumptions are made.

We consider the CH$_3$Y data first, and we remind the reader that we are using the sign convention for an electron affinity as given in Section 1. The AE values of Y$^-$ from CH$_3$Y (Table 8) are used with the IE of the CH$_3$ radical (9.84 ± 0.01 eV [89]) and the EA of the respective halogen atom (F (3.40 eV); Cl (3.61 eV); Br (3.36 eV) [90]) for the C–Y bond dissociation energy. For the C–H energy, we use the IE of the H atom (13.61 eV [36]) and the EA of the respective counter radical (CH$_2$F (0.25 ± 0.18 eV), CH$_2$Cl (0.74 ± 0.16 eV) and CH$_2$Br (0.79 ± 0.14 eV) [91–93]). The resulting upper limits to bond dissociation energies are shown in Table 9, and compared with literature values [64]. Note that an alternative way to present the data for the H–CH$_2$Y bonds is to use literature values for the bond dissociation energies, and calculate a lower limit to the electron affinity of the CH$_2$Y radical. We then obtain EA(CH$_2$F) ≥ −0.20 ± 0.2 eV, EA(CH$_2$Cl) ≥ 0.75 ± 0.2 eV and EA(CH$_2$Br) ≥ 0.93 ± 0.2 eV, all consistent within error limits of the literature values [91–93]. With the possible exception of the Br–CH$_3$ data where the values for $D_{298}$ are slightly outside error limits, there is excellent consistency between the upper-limit values for $D_{298}^\circ(Y–CH_3)$ and $D_{298}^\circ(H–CH_2Y)$ obtained indirectly from this ion-pair work and the accepted literature values. Furthermore, the significant difference between the upper limit for $D_{298}^\circ(F–CH_3)$ from this work, 5.84 ± 0.02 eV, and the literature value, 4.77 ± 0.09 eV, is in excellent agreement with the large kinetic energy of over 1 eV measured in the CH$_3^+$ cation by Locht et al. [96] for reaction (30) by ion kinetic energy analysis in photoionisation mass spectrometry. It is also interesting to note that the upper-limit value for both $D_{298}^\circ(Y–CH_3)$ and $D_{298}^\circ(H–CH_2Y)$ tends towards the literature value as the size of Y increases from F to Br. This trend is also observed in the data for the CF$_3$X series, see below. As the size of Y or X increases, the density of Rydberg states increases, increasing the likelihood of a Rydberg state crossing with an ion-pair state at as low an energy as thermochemically possible, thereby reducing the inequality presented in Equation (II) ultimately to an equality.

We next consider the CF$_3$X (X = Cl, Br, I) data. The atomic anion thresholds were not measured with the high resolution which was performed with the CH$_3$Y series, so the errors in the upper limits to the bond energies, ±0.2 eV are correspondingly higher. The AE of F$^−$ and Cl$^−$ from CF$_3$Cl, F$^−$ and Br$^−$ from CF$_3$Br, and F$^−$ and I$^−$ from CF$_3$I (Table 6) can be used to determine upper limits to the bond energies at 298 K of F–CF$_2$Cl, Cl–CF$_3$, F–CF$_2$Br, Br–CF$_3$, F–CF$_2$I and I–CF$_3$, respectively. Note that the Br$^−$ data from CF$_3$Br may not be strictly valid, since formation of this anion is probably dominated by the dissociative electron attachment mechanism. The calculations of these values follow the same procedure as explained in the previous paragraph for the CH$_3$Y series. Thus to calculate $D_{298}^\circ(X–CF_3)$, we use the EA value of the CF$_3$ radical, 1.82 ± 0.05 eV [97], and IE values for Cl (12.97 eV), Br (11.82 eV) and I (10.45 eV) [36]. In addition $D_{298}^\circ(F–CF_3)$ is calculated from the AE(F$^−$/CF$_4$), Section 5, and is also included in Table 9. Now the calculation is slightly different because CF$_3^−$ was not observed from CF$_4$, but the AE(F$^−$/CF$_4$) can be used to yield the same information if EA(F) = 3.40 eV and IE(CF$_3$) = 9.04 ± 0.04 eV are used instead [98]. Again, the consistency is noted between upper limit values for $D_{298}^\circ(X–CF_3)$ obtained indirectly from this ion-pair work and the
Table 9. Upper limits to experimentally determined bond dissociation energies and comparison with literature values.

<table>
<thead>
<tr>
<th>Bond</th>
<th>This work</th>
<th>Literature valuea</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–CH₃</td>
<td>4.21 ± 0.11</td>
<td>4.553 ± 0.004</td>
</tr>
<tr>
<td>F–CH₃</td>
<td>≤ 5.84 ± 0.02b</td>
<td>4.77 ± 0.09</td>
</tr>
<tr>
<td>Cl–CH₃</td>
<td>≤ 3.81 ± 0.02b</td>
<td>3.63 ± 0.02</td>
</tr>
<tr>
<td>Br–CH₃</td>
<td>≤ 2.98 ± 0.02b</td>
<td>3.05 ± 0.02</td>
</tr>
<tr>
<td>H–CH₃F</td>
<td>≤ 4.84 ± 0.2c</td>
<td>4.39 ± 0.04</td>
</tr>
<tr>
<td>H–CH₃Cl</td>
<td>≤ 4.33 ± 0.2c</td>
<td>4.34 ± 0.02</td>
</tr>
<tr>
<td>H–CH₃Br</td>
<td>≤ 4.28 ± 0.2c</td>
<td>4.43 ± 0.02</td>
</tr>
<tr>
<td>F–CF₃</td>
<td>≤ 7.4 ± 0.2d</td>
<td>5.67 ± 0.02</td>
</tr>
<tr>
<td>Cl–CF₃</td>
<td>≤ 4.4 ± 0.2e</td>
<td>3.79 ± 0.04</td>
</tr>
<tr>
<td>Br–CF₃</td>
<td>≤ 3.6 ± 0.2e</td>
<td>3.07 ± 0.01</td>
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<tr>
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<td>2.35 ± 0.01</td>
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<td>5.30f</td>
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<tr>
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<td>≤ 14.5–IE(SF₄CF₃)</td>
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<tr>
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<td>3.70m</td>
</tr>
<tr>
<td>Cl–SF₅</td>
<td>≤ 4.4 ± 0.3</td>
<td>2.54m</td>
</tr>
</tbody>
</table>

Notes: 

aReference [64].

bCalculated from the AE of Y⁻ formation from CH₃Y. The compound errors have contributions from the errors in AE(Y⁻), typically 0.02 eV, and the error in IE(CH₃), 0.01 eV.

cCalculated from the AE of CH₂Y⁻ formation from CH₃Y, in Figures 15–17. The errors are dominated by errors in AE (CH₂Y⁻), typically 0.2 eV.

dCalculated from the AE(F⁻) from CF₄ [17].

eCalculated from the AE of X⁻ formation from CF₃X.

fError not quoted.

gCF₃ and SF₅ are either not observed, or are not formed by ion-pair formation.

hUses an enthalpy of formation of SF₄Cl⁺ of +327 kJ mol⁻¹ [69].

iCalculated assuming the enthalpies of formation at 298 K of the CF₂Br and CF₂I radicals are −238 and −144 kJ mol⁻¹, respectively [94,95].

jValue at 0 K [56].

kCalculated assuming formation of SF₃Cl and SF₅ are −761 and −915 kJ mol⁻¹, respectively [69]. Errors are often not quoted and difficult to estimate, but probably an error in the bond energy of ±0.20 eV is realistic.

accepted literature values. Furthermore, as described in the preceding paragraph, the upper limit value for $D_{298}^e$ tends towards the accurate value as the size of X increases from F to I. The data for the bond energy of F–CF₂X is incomplete because the IE of the CF₂Br and CF₂I radicals are unknown.

The formation of F⁻ from CF₃I at onset arises from the dissociation reaction CF₃I → F⁻ + CF₂I⁺. Although an upper limit to $D_{298}^e$(F–CF₂I) cannot be calculated, as
described above, the information is available to calculate an upper limit to $D_{298}^{o}(F-CF_{2}I^+)$ if Equation (XIV) is used,

$$AE_{298}(F^-) \geq IE(CF_{3}I) + D_{298}^{o}(F-CF_{2}I^+) - EA(F).$$  \hspace{1cm} \text{(XIV)}$$

The $AE_{298}(F^-)$ is $9.7 \pm 0.2 \text{ eV}$ (Table 6) and the $IE(CF_{3}I)$ is $10.37 \text{ eV}$ [78], giving $D_{298}^{o}(F-CF_{2}I^+) \leq 2.7 \pm 0.2 \text{ eV}$ or $263 \pm 19 \text{ kJ mol}^{-1}$. Since $D_{298}^{o}(F-CF_{2}I^+)$ is simply the enthalpy change for reaction (38),

$$CF_{3}I^+ \rightarrow CF_{2}I^+ + F \quad \Delta_{r}H_{298}^{o} \leq 263 \pm 19 \text{ kJ mol}^{-1}$$  \hspace{1cm} \text{(38)}$$

an upper limit to $\Delta_{r}H_{298}^{o}(CF_{2}I^+)$ can be determined. Thus using standard values for $CF_{3}I^+$ and F, $\Delta_{r}H_{298}^{o}(CF_{2}I^+)$ is calculated to be $\leq 598 \pm 20 \text{ kJ mol}^{-1}$. A similar calculation for $F^-$ from $CF_{3}Br$ yields $D_{298}^{o}(F-CF_{2}Br^+) \leq 6.47 \pm 0.21 \text{ eV}$ and $\Delta_{r}H_{298}^{o}(CF_{2}Br^+) \leq 1017 \pm 25 \text{ kJ mol}^{-1}$. This latter value is consistent with a more accurate way of determining the enthalpy of formation of $CF_{2}Br^+$ from cleavage of the weakest bond in $CF_{2}Br_2$. Thus using threshold photoelectron photoion coincidence spectroscopy at the relatively modest resolution of ca. 0.03 eV, a more accurate upper limit value of $570 \pm 9 \text{ kJ mol}^{-1}$ at 298 K was obtained [99].

Finally, we note that the top half of Table 9 includes datum for the H–CH$_3$ bond energy from the $AE_{298}(H^-)$ from CH$_4$ [19]. The signal at threshold, 13.3 ± 0.1 eV, corresponds to direct ion-pair formation. This onset lies well above the first adiabatic IE of methane, 12.61 eV [100], but well below the second adiabatic IE, 22.39 eV [101]. The H$^-$ peak at 15 eV, with onset at 13.3 eV, cannot therefore coincide with a Rydberg state of CH$_4$, and its broad shape and slow onset indicate direct ion-pair formation. Under these circumstances, given sufficient sensitivity in the experiment, the H$^-$ signal from CH$_4$ should turn on at the thermochemical onset. The H–CH$_3$ bond energy determined from the H$^-$ onset, 4.21 ± 0.11 eV, is, however, slightly less than the well-established literature value of 4.553 ± 0.004 eV [64]. This scientific impossibility could be accounted for by uncertainties in the thermochemistry, but more likely by contributions to the H$^-$ signal from hot bands of CH$_4$ and/or by the presence of vibrationally excited molecules possibly caused by electron excitation by photoelectrons. The bottom half of Table 9 completes the data for the other molecules studied in detail by ion-pair spectroscopy: SF$_6$, CF$_4$, SF$_3$CF$_3$ and SF$_2$Cl. Whilst there are no real surprises in the data, and one would not use this as the method of choice to determine the bond dissociation energy of a neutral molecule, it is satisfying that all the data for the experimentally determined and literature values of $D_{298}^{o}(A-BC)$ are consistent. It is more likely that this method could be used to determine a lower limit for the EA of the radical A, assuming that both the values of $D_{298}^{o}(A-BC)$ and IE(BC) are known.

8. General comments on ion-pair formation in polyatomic molecules

The systems already described plus CH$_2$X$_2$, CF$_2$Y$_2$, CCl$_2$Z$_2$; CHX$_3$, CFY$_3$, CClZ$_3$; C$_x$H$_y$ and C$_m$F$_n$

The results presented in Section 6 represent a minority of the polyatomic molecules in the gas phase that have been studied by VUV anion spectroscopy since 2005 at the Daresbury synchrotron source. In total, 24 molecules have been studied. Data for the 11 molecules reported so far in this review plus the remaining 13 molecules (C$_2$H$_4$, C$_2$H$_6$, International Reviews in Physical Chemistry 243

Downloaded By: [Tuckett, Richard] At: 08:46 10 June 2011
C₃H₈, C₂F₄, C₂F₆, C₃F₈, CH₂F₂, CHF₃, CH₂Cl₂, CHCl₃, CCl₄, CF₂Cl₂ and CFCl₃) are collected in Table 10, and the spectra of these 13 molecules are shown in Figures 20–32. Full details can be found in the PhD thesis of one of the authors [22]. This forms the most comprehensive collection of information about anion formation, of which ion-pair formation is a particular example, from polyatomic molecules since the Berkowitz [1] review. Some of these molecules (CF₄, SF₆, CH₄, CH₃Y, CF₅Cl, C₂H₄, C₂H₆, C₃H₈) have previously been studied by the groups of Mitsuke and Baumgärtel [6–10,74,79]. All our work is in excellent agreement with these studies, but in most cases the enhanced signal-to-noise ratio of the spectra, the larger number of anions observed and the addition of absolute cross-sections and quantum yields represent a significant improvement. These data have not yet all been analysed in full, but certain trends are emerging which are described in this section.

8.1. Appearance energies of anions and thermochemical thresholds

First, we compare the experimental appearance energy (AE₂⁹⁸) for anion formation, usually by ion-pair formation, with the thermochemically determined threshold (Δ_rH²⁹⁸ for the relevant anion-forming dissociation reaction). We remind the reader that for the generic polyatomic molecule ABC,

\[
\text{AE}_{298}(A^-) \geq D_r^0(A-BC) + IE(BC) - EA(A),
\]

or

\[
\geq IE(ABC) + D_r^0(A-BC^+) - EA(A),
\]

or

\[
\geq \Delta_rH_{298}^o(ABC \rightarrow A^- + BC^+).
\]

The equality of these equations only holds true in the absence of a kinetic shift and/or a barrier in the exit channel. These data are shown in columns 4 and 6 of Table 10, and we reiterate that at our experimental resolution we are working within the approximation that energy and enthalpy changes are one and the same (Section 3). Thus, AE₂⁹⁸(A⁻) must be greater than or equal to Δ_rH²⁹⁸, and this is indeed true for the majority of the results shown in Table 10. For the few instances where this inequality is not obeyed (e.g. H⁻ from CH₄), thermal effects, the presence of vibrationally excited molecules and/or uncertainty in the calculated Δ_rH²⁹⁸ values are expected to be responsible. In most cases, when only one dissociation process is thermodynamically accessible, the reaction occurring at the AE₂⁹⁸ value can unambiguously be identified to single bond-breaking ion-pair dissociation. Multiple-bond-breaking ion-pair reactions are assigned more tentatively, assuming the process yielding the least amount of excess energy prevails (e.g. CF₃Cl → Cl⁻ + CF₂⁺ + F⁻ rather than CF₃Cl → Cl⁻ + CF₃⁺). This assumption is justified by experimental observations: it is common for the appearance of a feature in an ion-pair spectrum to correlate with a possible dissociation threshold.

The difference between AE₂⁹⁸ and Δ_rH²⁹⁸ is plotted in Figure 33(a) for all anions listed in Table 10 that result from single bond-breaking ion-pair dissociation. Quite arbitrarily, this energy difference is plotted as a function of the mass of the parent molecule.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>AIE(^a) (eV)</th>
<th>Anion</th>
<th>AE(_{298})(^b) (eV)</th>
<th>Reaction at AE(_{298})(^c)</th>
<th>(\Delta_{f}H_{298}^{d}) (eV)</th>
<th>(\sigma_{\text{max}}^{e}) (cm(^2))</th>
<th>(E(\sigma_{\text{max}}^{f})) (eV)</th>
<th>(\Phi(\sigma_{\text{max}}^{g}))</th>
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<tbody>
<tr>
<td>CH(_4)</td>
<td>12.61</td>
<td>H(^-)</td>
<td>13.30 ± 0.10</td>
<td>CH(_4) → H(^-) + CH(_3)^+</td>
<td>13.7</td>
<td>1.4 × 10(^{-22})</td>
<td>20.6</td>
<td>4.4 × 10(^{-6})</td>
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<tr>
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<td>H(^-)</td>
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<td>8.3 × 10(^{-22})</td>
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<td>1.4 × 10(^{-5})</td>
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<tr>
<td>C(_2)H(_6)</td>
<td>11.52</td>
<td>H(^-)</td>
<td>12.00 ± 0.10</td>
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<td>19.3</td>
<td>2.7 × 10(^{-5})</td>
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<td>C(_3)H(_8)</td>
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<td>H(^-)</td>
<td>13.2 ± 0.2</td>
<td>C(_3)H(_8) → H(^-) + C(_3)H(_7)^+</td>
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<td>3.3 × 10(^{-21})</td>
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<td>CF(_4)</td>
<td>15.4</td>
<td>F(^-)</td>
<td>13.0 ± 0.2</td>
<td>CF(_4) → F(^-) + CF(_3)^+</td>
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<td>1.4 × 10(^{-21})</td>
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<td>C(_2)F(_4)</td>
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<td>13.17 ± 0.05</td>
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<td>1.7 × 10(^{-23})</td>
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<td>2.0 × 10(^{-7})</td>
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<td>13.1 ± 0.2</td>
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<td>12.53</td>
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<td>1.4 × 10(^{-21})</td>
<td>16.0</td>
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<th>Reaction at $AE_{298}^c$</th>
<th>$\Delta H_{298}^o$ (eV)</th>
<th>$\sigma_{\text{max}}^a$ (cm$^2$)</th>
<th>$E(\sigma_{\text{max}})^f$ (eV)</th>
<th>$\Phi(\sigma_{\text{max}})^g$</th>
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<td>11.2 ± 0.2</td>
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<td>9.26 ± 0.05</td>
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<td>7.0 × 10$^{-21}$</td>
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<td>–</td>
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<td>1.8 × 10$^{-4}$</td>
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<th>Reaction at AE_{298}</th>
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<td>I^-</td>
<td>8.8 ± 0.2</td>
<td>CF_3I + I^- + CF_3I^+</td>
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<td>_m</td>
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<td></td>
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<td>CF^-</td>
<td>21.6 ± 0.2</td>
<td>CF_3I + CF^- + I^- + CF</td>
<td>_</td>
<td>1.1 × 10^{-22}</td>
<td>23.6</td>
<td>_m</td>
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<td>SF_6</td>
<td>15.116</td>
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<td>12.7 ± 0.2</td>
<td>SF_6 + F^- + SF_6^+</td>
<td>10.4</td>
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<td>14.2</td>
<td>2.4 × 10^{-4}</td>
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<td>16.3 ± 0.2</td>
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<td>14.1</td>
<td>1.4 × 10^{-22}</td>
<td>18.3</td>
<td>1.9 × 10^{-6}</td>
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<td>12.3</td>
<td>F^-</td>
<td>12.7 ± 0.2</td>
<td>[SF_6 + e^- + F + SF_5^-]</td>
<td>_</td>
<td>6.1 × 10^{-20}</td>
<td>14.1</td>
<td>_m</td>
</tr>
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<td></td>
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<td>Cl^-</td>
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<td>_</td>
<td>_</td>
<td>10.9</td>
<td>_</td>
</tr>
<tr>
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<td>F^-</td>
<td>11.05 ± 0.05</td>
<td>SF_3CF_3 + F^- + CF_3^+ + SF_4</td>
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<td>3.4 × 10^{-20}</td>
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<td>3.4 × 10^{-4}</td>
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<td></td>
<td></td>
<td>F_2^-</td>
<td>16.1 ± 0.2</td>
<td>SF_3CF_3 + F_2^- + CF_3^+ + SF_4</td>
<td>14.3</td>
<td>1.2 × 10^{-21}</td>
<td>17.9</td>
<td>1.1 × 10^{-5}</td>
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<tr>
<td></td>
<td></td>
<td>SF^-</td>
<td>24.0 ± 0.2</td>
<td>SF_3CF_3 + SF^- + CF_3^+ + 4F</td>
<td>23.0</td>
<td>2.8 × 10^{-22}</td>
<td>28.8</td>
<td>2.4 × 10^{-6}</td>
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<td>SF_3CF_3 + SF_2^- + CF_3^+ + 3F</td>
<td>20.0</td>
<td>3.9 × 10^{-22}</td>
<td>24.2</td>
<td>2.5 × 10^{-6}</td>
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<tr>
<td></td>
<td></td>
<td>SF_3^-</td>
<td>15.4 ± 0.2</td>
<td>SF_3CF_3 + SF_3^- + CF_3^+ + 2F</td>
<td>16.0</td>
<td>1.0 × 10^{-20}</td>
<td>17.6</td>
<td>1.0 × 10^{-4}</td>
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<tr>
<td></td>
<td></td>
<td>SF_4^-</td>
<td>13.0 ± 0.2</td>
<td>SF_3CF_3 + SF_4^- + CF_3^- + F</td>
<td>13.4</td>
<td>1.3 × 10^{-20}</td>
<td>14.1</td>
<td>1.7 × 10^{-4}</td>
</tr>
</tbody>
</table>

Notes: 
- "AIE" values are taken from the following sources: CH_4 [100]; C_2H_4 [102]; C_2H_6 [103]; C_3H_8 [104]; CF_4 [48]; CF_2H [105]; C_2F_6 [106]; C_2F_8 [106]; CH_2F [85]; CH_2F_2 [63]; CHF_3 [107]; CH_3Cl [85]; CH_3Cl_2 [108]; CHCl_3 [109]; CCl_4 [63]; CF_2Cl [77]; CF_2Cl_2 [110]; CFCl_3 [109]; CH_3Br [86]; CF_3Br [77]; CF_3I [78]; SF_6 [40]; SF_3Cl [68]; SF_3CF_3 [42].
- Experimentally determined appearance energy at 298 K.
- Reaction occurring at onset.
- Δ_H_{298} for the reaction in column 5, calculated from standard enthalpies of formation.
- Absolute value for the ion-pair cross-section (σ) at its maximum.
- Energy (E) at which the ion-pair cross-section reaches its maximum.
- Quantum yield (Φ) for ion-pair formation at E (σ_{max}). The ion-pair cross-section is divided by the total photoabsorption cross-section. Data for σ_{abs} from the following sources (for molecules not listed here see references in column 1): C_2H_4 [111]; C_2H_6 [112]; C_3H_8 [112]; CH_2F_2 [113]; CHF_3 [75];
(Table 10 footnote continued)

CH₂Cl₂ [114]; CHCl₃ [115]; CCl₄ [75]; CF₂Cl₂ [113]; CFCl₃ [115].

Data for this molecule are presented in Section 8 and Figures 20–32.

Data in columns 3–9 for CF₄, SF₆ and SF₆CF₃ are taken from Section 5 and Table 2.

The reaction occurring at the AE for this anion is not known due to the many different dissociation channels that are thermochemically open.

Ion-pair quantum yield cannot be calculated because $\sigma_{abs}$ is not known over the required energy range.

Total photoabsorption cross-section for C₂F₆ is reported from 16–62 eV and so $\Phi(\sigma_{max})$, at 14.7 eV, cannot be calculated. However, $\Phi$ for F⁻ formation at 17.7 eV is $4.8 \times 10^{-5}$ [$\sigma_{abs}$ (C₂F₆, 17.7 eV) = $7.3 \times 10^{-17}$ cm²] [50].

H⁻ detected at m/z 1, but the signal was significantly weaker than the dominant anion. The H⁻ ion yield matches that of the dominant anion, presumably because of the zero-blast effect in the QMS [35], and cannot therefore be trusted.

H⁻ detected at m/z 1, but the signal was of similar intensity to that of other anions. The H⁻ ion yield is unique, but it may contain contributions from other anions due to the zero-blast effect [35]. Only limited information can therefore be obtained. For example, absolute cross-sections cannot be determined for H⁻ ion-pair formation unless it is the dominant anion [19,20].

The fact that $\Delta H_{298}$ exceeds AE₂₉₈ may result from other anions being detected due to the zero-blast effect (see notes p and q), giving an AE lower than it should be. Alternatively, thermal effects (i.e. hot bands) could cause the AE₂₉₈ to precede $\Delta H_{298}$.

$\Delta_f H_{298}$ is not known for CCl⁻, FCI⁻ and FBr⁻.

Anion signal increases non-linearly with increasing parent gas pressure. Anion production is dominated by a two-step electron attachment process where photoionisation provides the source of electrons. All molecules have fast thermal electron attachment rate coefficients exceeding $10^{-8}$ cm³ molecule⁻¹ s⁻¹.

Data in columns 3–9 for CH₃Y molecules (Y = F, Cl, Br) are taken from Section 6.3 and Table 8.

Data in columns 3–9 for CFₓX molecules (X = Cl, Br, I) are taken from Section 6.2 and Table 6.

Data in columns 3–9 for SF₅Cl are taken from Section 6.1.

The I⁻ yield at $E \geq 10.4$ eV is dominated by dissociative electron attachment to CF₃I (see note u). However, below 10.4 eV the observed I⁻ signal can only arise by ion-pair dissociation. Using absorption cross-sections from Eden et al. [76], the cross-section for I⁻ formation at 9.0 eV is $3.8 \times 10^{-21}$ cm² with a corresponding quantum yield of $8 \times 10^{-5}$.
The random distribution of points in this graph is probably to be expected. However, if the points for H\(^-\) and F\(^-\) ions are plotted separately (Figure 33(b) and (c), respectively), the distributions show an interesting trend; the points for H\(^-\) ions are clustered around \((\Delta E_{298} - \Delta_r H_{298}^o) = 0\), whilst those for F\(^-\) take larger values. This indicates that the dynamics for H\(^-\) ion-pair formation tend to allow for this anion to ‘turn on’ at the thermochemical threshold, favouring dissociation with low excess energy release. It is also interesting that the anion is H\(^-\) for four out of the five instances in Figure 33(a) where \((\Delta E_{298} - \Delta_r H_{298}^o) < 0\), the other being for Br\(^-\) from CH\(_3\)Br with a value of \(-0.04\) eV. By contrast, F\(^-\) ion pairs are formed with larger excess energies in the range 0.7–2.5 eV. These trends become even clearer when the dataset is limited to methane and the halo-substituted methanes (Figure 33(d)–(g)), where the data for Cl\(^-\) and CY\(_3\) (i.e. CF\(_3\), CH\(_2\)F\(^-\), CH\(_2\)Cl\(^-\) and CH\(_3\)Br\(^-\)) anions are isolated and plotted. Low excess energies are always observed for CY\(_3\) anion formation; all points in Figure 33(g) have values for \((\Delta E_{298} - \Delta_r H_{298}^o)\) between 0 and 0.6 eV. In Figure 33(e) and (f), for F\(^-\) and Cl\(^-\) ions from halo-substituted methanes, an apparent positive correlation between \((\Delta E_{298} - \Delta_r H_{298}^o)\) and the mass of the parent molecule is observed. This is surprising given that the data were plotted against mass for no particular reason, other than to observe the scattering of \((\Delta E_{298} - \Delta_r H_{298}^o)\) about the y-axis. Indeed, the same correlation is observed if the x-axis represents the total number of

Figure 20 (colour online). Cross-section for formation of H\(^-\) from C\(_2\)H\(_4\) in the range 12–35 eV. The spectrum was recorded with a wavelength resolution of 0.6 nm and a step size of 0.05 eV. The appearance energy, 13.06 eV, was determined from a higher resolution scan, recording the onset region with a resolution of 0.2 nm and a step size of 0.02 eV.
electrons in the molecule, or the molecular polarisability. There is no obvious explanation for this observation and ideally more data points are required if this trend is to be confirmed.

8.2. Ion-pair formation below the ionisation energy

From an experimental point of view it is advantageous to detect ion pairs below the ionisation energy of the parent molecule; signal will then be observed against a zero
background, and anions or cations can be detected with the confidence that they must originate from ion-pair formation. Energetically, it is possible for ion-pair formation to occur below the IE(ABC) if, for the generic reaction $ABC \rightarrow A^- + BC^+$, the electron affinity of $A$ exceeds the bond dissociation energy of $A^-BC^+$ (as discussed in Section 1). This condition is most likely satisfied when $A$ is a halogen atom with a corresponding large value for its $EA$. Indeed, *theoretically*, this is true for every halogen-containing molecule in

Figure 22 (colour online). Cross-section for formation of $H^-$ from $C_3H_8$: (a) in the range 12–28 eV with a step size of 0.05 eV and a resolution of 0.6 nm; (b) two separate scans covering the range 12–24 eV at improved resolution, from 12.0 to 17.5 eV recorded with a step size of 0.02 eV and a wavelength resolution of 0.2 nm, and from 16–24 eV recorded with a step size of 0.01 eV and a resolution of 0.12 nm. The appearance energy, 13.2 eV, is indicated.
Figure 23 (colour online). Yields of anions from VUV photoexcitation of C$_2$F$_4$: (a) F$^-$ absolute cross-sections in the range 13–32 eV, the scan recorded with a step size of 0.05 eV and a wavelength resolution of 0.6 nm, (b) three higher resolution F$^-$ scans covering the range 12.7–20.4 eV, all with a step size of 0.01 eV and a resolution of 0.2 nm. The appearance energy of F$^-$, 13.17 eV, is indicated. (c) Yield of CF$^-$ in the range 21–32 eV recorded with a step size of 0.1 eV and a resolution of 0.6 nm.
Table 10, with one exception: \( F^- \) from \( C_2F_4 \). Since the EA(F) is 3.40 eV, the IE(\( C_2F_4 \)) is 10.12 eV and the AE(\( F^- \)) is 13.17 eV (Table 10), we deduce that \( 3.40 < D_{298}^0 (F-C_2F_3^+) < 6.45 \) eV. This is consistent with the value of \( 5.7 \pm 0.2 \) eV from thermochemistry (Table 11, Column 2). The unsaturated, perfluorinated molecule \( C_2F_4 \) is a classic example of the ‘perfluoro effect’ [23]; the C–F bonds in \( C_2F_4 \) are strengthened by the combined inductive effect of four fluorine atoms at the expense of a significantly weakened C= C bond. Thus the \( F-C_2F_3 \) bond dissociation energy, \( 5.66 \pm 0.13 \) eV is greater than the H–C2H3 energy, \( 4.81 \pm 0.03 \) eV [64]. Bond dissociation energies for ionised and neutral molecules described in this review are shown in Table 11. However, the observation of ion-pair formation below the IE is not always restricted to instances where A is a halogen atom. Despite the small EA of the hydrogen atom, \( 0.754 \) eV [90], \( H^- \) ions are observed below the IE for three out of the eleven hydrogen-containing molecules listed in Table 10: \( CH_2F_2, CHF_3 \) and \( CHCl_3 \). For these three molecules, \( D'^0(H-CHF_2^+ \) or \( H-CX_3^+) < 0.754 \) eV (see Table 11).

From the data in Table 10, there are only four instances where the maximum value of the cross-section, \( \sigma_{\text{max}} \), was observed below the IE of the parent molecule: \( F^- \) from \( CF_4 \), \( Cl^- \) from \( CH_2Cl_2 \), \( Br^- \) from \( CH_3Br \), and \( F^- \) from \( SF_6 \). In all other cases, \( \sigma_{\text{max}} \) was observed at a photon energy above the IE. It is also worth noting that, for the majority of the 24 molecules studied, \( \sigma_{\text{max}} \) for producing atomic anions occurs between 16 and 22 eV, which is enough energy to access multiple-bond-breaking ion-pair dissociation channels. Exceptions to this are for \( CF_4, C_2F_6, SF_6, SF_5Cl, CH_3F, CH_3Cl, CH_2Cl_2 \) and \( CH_3Br \), where the lowest energy ion-pair dissociation reaction occurs at the cross-section maximum.

Figure 24 (colour online). Cross-section for formation of \( F^- \) from \( C_2F_6 \) in the range 13–32 eV with a step size of 0.02 eV and a wavelength resolution of 0.2 nm. The appearance energy, 13.62 eV, is indicated.
Figure 25 (colour online). Yield of anions from photoexcitation of C₃F₈. (a) F⁻ absolute cross-sections in the range 12–30 eV, the scan recorded with a step size of 0.05 eV and a wavelength resolution of 0.6 nm. (b) F⁻ spectrum covering the range 19.5–22.5 eV range with a step size of 0.01 eV and a resolution of 0.12 nm. (c) F⁻ spectrum covering the range 22.5–26.0 eV range with a step size of 0.01 eV and a resolution of 0.12 nm. The appearance energy of F⁻, 13.1 eV, is indicated. (d) Yield of CF₂⁻ in the range 19–26 eV recorded with a step size of 0.1 eV and a resolution of 0.6 nm.
Figure 26 (colour online). Ion yields for anions observed following photoexcitation of CH$_2$F$_2$. (a) H$^-$ ion yield in the range 11.5–30.0 eV recorded with a step size of 0.02 eV and a wavelength resolution of 0.2 nm. Due to the zero-blast effect in the QMS, the signal detected at this m/z value of 1 may also contain contributions from other ions present (i.e. F$^-$ and F$_2^-$). An absolute cross-section cannot therefore be determined, and it is possible that the observed features do not all result exclusively from H$^-$ anions. (b) Higher resolution scan of H$^-$ covering the range 12.0–13.7 eV recorded with a step size of 0.005 eV and a resolution of 0.1 nm. A similar scan of the peak at 12.56 eV in the F$^-$ spectrum was structureless and did not reproduce that in (b) for H$^-$. (c) Yield and cross-section for F$^-$ in the range 11.5–30.0 eV recorded with a step size of 0.02 eV and a resolution of 0.2 nm. (d) Yield and cross-section for F$_2^-$ in the range 16.5–25.5 eV recorded with a step size of 0.02 eV and a resolution of 0.2 nm. For all three anions, the appearance energies are indicated.
8.3. Quantum yields for anion formation

The quantum yield values, $\Phi$, in Column 9 of Table 10 represent the probability for the formation of a given anion via an ion-pair reaction following the absorption of a photon by the parent molecule. Its value is calculated by dividing the anion cross-section by the total photoabsorption cross-section. A quantum yield value is always quoted at a given energy. Each quantum yield listed in the table represents the maximum value calculated within the energy range studied. The largest value is $2.3 \times 10^{-3}$ or 0.23 % (for both $F^-$ from CH$_3$F and Cl$^-$ from CH$_3$Cl) and the smallest is $5.6 \times 10^{-7}$ or 0.000056 % (for F$_2^-$ from CF$_4$). The majority of the quantum yields lie between $5 \times 10^{-4}$ and $1 \times 10^{-6}$ (i.e. 0.05–0.0001%).

Figure 27 (colour online). Ion yields for anions observed following photoexcitation of CHF$_3$. The appearance energies of H$^-$ and CF$_3^-$ are indicated. (a) H$^-$ ion yield in the photon energy range 12–25 eV recorded with a step size of 0.02 eV and a wavelength resolution of 0.3 nm. As in Figure 26, the signal at $m/z$ 1 may also contain contributions from other ions present (i.e. F$^-$ and CF$_3^-$), so the absolute cross-section values cannot be determined. (b) Yield and cross-section for F$^-$ in the range 12–25 eV recorded in four separate scans: (i) dotted line, 12.0–15.3 eV, with a step size of 0.1 eV and a resolution of 0.6 nm; (ii) solid line, 15.3–18.1 eV, with a step size of 0.01 eV and a resolution of 0.2 nm; (iii) solid line, 18.4–22.3 eV, with a step size of 0.01 eV and a resolution of 0.16 nm; (iv) solid line, 22.8–24.4 eV with a step size of 0.005 eV and a resolution of 0.12 nm. The rise in signal of F$^-$ for $h\nu < 12.4$ eV arises from second-order radiation, since a scan from 8 to 12 eV using a LiF window showed only background signal. (c) Yield and cross-section for CF$_3^-$ in the range 12–27 eV recorded with a step size of 0.1 eV and a resolution of 0.6 nm.
Figure 28 (colour online). Ion yields for anions observed following photoexcitation of CH$_2$Cl$_2$. (a) H$^-$ ion yield in the range 11–30.0 eV recorded with a step size of 0.02 eV and a wavelength resolution of 0.2 nm. As in Figures 26 and 27, the H$^-$ signal may also contain contributions from other ions present (i.e. Cl$^-$ and Cl$_2^-$), so its absolute cross-section cannot be determined. (b) Yield and cross-section for Cl$^-$ in the range 9–30 eV recorded with a step size of 0.02 eV and a resolution of 0.2 nm. (c) Higher resolution Cl$^-$ scan from 9.0 to 12.5 eV recorded with a step size of 0.01 eV and a resolution of 0.12 nm. (d) Yield and cross-section for Cl$_2^-$ in the range 12–18 eV recorded with a step size of 0.02 eV and a resolution of 0.2 nm. For all three anions, the appearance energies are indicated.
Figure 29 (colour online). Ion yields for anions observed following photoexcitation of CHCl₃. (a) Three separate scans are merged to generate the H⁻ ion yield: (i) from 8 to 15 eV with a step size of 0.05 eV and a wavelength resolution of 0.6 nm; (ii) from 15.0 to 19.5 eV with a step size of 0.02 eV and a resolution of 0.2 nm; (iii) from 19.5 to 32.0 eV with a step size of 0.05 eV and a resolution of 0.6 nm. The H⁻ signal may contain contributions from other ions present (i.e. CH⁻, Cl⁻ and CCl⁻). (b) Yield and cross-section for Cl⁻ in the range 8–32 eV generated by merging three scans: (i) from 8.60 to 10.64 eV with a step size of 0.02 eV and a resolution of 0.4 nm; (ii) from 10.65 to 16.80 eV with a step size of 0.05 eV and a resolution of 0.6 nm; (iii) from 16.85 to 32.00 eV with a step size of 0.05 eV and a resolution of 0.6 nm. (c) Yield and cross-section for CH⁻ in the range 20–32 eV recorded with a step size of 0.05 eV and a resolution of 0.6 nm. (d) Yield and cross-section for CCl⁻ in the range 14–32 eV recorded with a step size of 0.1 eV and a resolution of 0.6 nm. For all four anions, the appearance energies are indicated.
Figure 30 (colour online). Ion yields for anions observed following photoexcitation of CCl₄. (a) Three scans have been merged to generate the Cl⁻ ion yield: (i) from 10.5 to 17.2 eV with a step size of 0.01 eV and a wavelength resolution of 0.2 nm; (ii) from 17.2 to 22.0 eV with a step size of 0.02 eV and a resolution of 0.2 nm; (iii) from 22 to 32 eV with a step size of 0.02 eV and a resolution of 0.2 nm. The Cl⁻ signal at 16.45 and 24.9 eV increases non-linearly with gas pressure; absolute cross-sections cannot be determined because the formation of Cl⁻ is dominated by the dissociative electron attachment. (b) TPES of CCl₄ [63], and the similarity of the peak positions with those in the Cl⁻ ion yield in (a) is noted. (c) Yield and cross-section for CCl⁻ in the range 20–32 eV recorded with a step size of 0.05 eV and a resolution of 0.6 nm. For both anions, the appearance energies are indicated.
Figure 31 (colour online). Ion yields for anions observed following photoexcitation of CF₂Cl₂. (a) Two scans have been merged to generate the yield and cross-section for F⁻: (i) from 10.0 to 17.7 eV with a step size of 0.02 eV and a wavelength resolution of 0.2 nm; (ii) from 17.7 to 30.0 eV with a step size of 0.05 eV and a resolution of 0.6 nm. (b) Likewise, two scans have been merged to generate the yield and cross-section for Cl⁻: (i) from 10.0 to 12.5 eV with a step size of 0.01 eV and a resolution of 0.2 nm; (ii) from 13.9 to 32.0 eV with a step size of 0.05 eV and a resolution of 0.6 nm. (c) Yield and cross-section for CF⁻ formation in the range 20–30 eV recorded with a step size of 0.1 eV and a resolution of 0.6 nm. For all three anions, the appearance energies are indicated.
By comparing these data for the 24 molecules studied, some general statements can be made:

(a) Quantum yields for the production of an atomic anion are most often much greater than quantum yields for the production of a molecular anion. There are only a very few exceptions to this statement (e.g. CF$_3^-$ vs. F$^-$ formation from CHF$_3$).

Figure 32 (colour online). Ion yields for anions observed following photoexcitation of CFCl$_3$. (a) Two scans have been merged to generate the Cl$^-$ yield: (i) from 11 to 16 eV recorded with a step size of 0.02 eV and a wavelength resolution of 0.3 nm, and (ii) from 16 to 32 eV recorded with a step size of 0.05 eV and a resolution of 0.6 nm. The Cl$^-$ signal at 12.2, 18.2, 21.7 and 25.4 eV in all cases was shown to increase non-linearly with pressure of CFCl$_3$, so absolute cross-sections cannot be determined because the formation of Cl$^-$ is dominated by electron attachment. (b) Yield and cross-section for F$^-$ (which is formed by ion-pair formation) from 14 to 32 eV recorded with a step size of 0.05 eV and a resolution of 0.6 nm.
Figure 33 (colour online). (a) The distribution of (AE\textsubscript{298} – ΔH\textsubscript{298}) for all anions produced from a single bond-breaking ion-pair dissociation reaction (see Table 10). (b) The sub-set from (a) showing H\textsuperscript{−}, (c) the sub-set from (a) showing F\textsuperscript{−} anions. (d)–(g) Data extracted from (a) for methane and the halo-substituted methanes only. CY\textsubscript{n}\textsuperscript{−} in (g) includes data for CF\textsubscript{3}\textsuperscript{−}, CH\textsubscript{2}F\textsuperscript{−}, CH\textsubscript{2}Cl\textsuperscript{−} and CH\textsubscript{2}Br\textsuperscript{−}.

Table 11. Bond dissociation energies of cations, D\textsuperscript{c+}, and neutral polyatomic molecules, D\textsuperscript{0}, at 298 K.

<table>
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<th>Cation</th>
<th>D\textsuperscript{c+}\textsubscript{therm} \textsuperscript{a} (eV)</th>
<th>D\textsuperscript{c+}\textsubscript{expt} \textsuperscript{b} (eV)</th>
<th>Neutral</th>
<th>D\textsuperscript{0}\textsuperscript{c} \textsubscript{lit} \textsuperscript{c} (eV)</th>
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<td>H–C\textsubscript{2}H\textsubscript{3}\textsuperscript{+}</td>
<td>2.7 ± 0.3</td>
<td>≤(3.3 ± 0.2)</td>
<td>H–C\textsubscript{2}H\textsubscript{4}</td>
<td>4.81 ± 0.03</td>
</tr>
<tr>
<td>H–C\textsubscript{2}H\textsubscript{3}\textsuperscript{+}</td>
<td>1.1 ± 0.1</td>
<td>≤(1.2 ± 0.2)</td>
<td>H–C\textsubscript{2}H\textsubscript{3}</td>
<td>4.36 ± 0.01</td>
</tr>
<tr>
<td>H–C\textsubscript{2}H\textsubscript{4}\textsuperscript{+}</td>
<td>1.6 ± 0.4</td>
<td>≤(3.1 ± 0.3)</td>
<td>H–C\textsubscript{3}H\textsubscript{7}</td>
<td>4.38 ± 0.02</td>
</tr>
<tr>
<td>H–CH\textsubscript{3}\textsuperscript{+}</td>
<td>1.8 ± 0.2</td>
<td>≤(1.4 ± 0.1)</td>
<td>H–CH\textsubscript{3}</td>
<td>4.553 ± 0.004</td>
</tr>
<tr>
<td>H–CH\textsubscript{2}F\textsuperscript{+}</td>
<td>0.9 ± 0.4</td>
<td>–\textsuperscript{d}</td>
<td>H–CH\textsubscript{2}F</td>
<td>4.39 ± 0.04</td>
</tr>
<tr>
<td>H–CH\textsubscript{2}Cl\textsuperscript{+}</td>
<td>1.8 ± 0.4</td>
<td>–\textsuperscript{d}</td>
<td>H–CH\textsubscript{2}Cl</td>
<td>4.34 ± 0.02</td>
</tr>
<tr>
<td>H–CH\textsubscript{3}Br\textsuperscript{+}</td>
<td>1.8 ± 0.4</td>
<td>≤(2.3 ± 0.2)</td>
<td>H–CH\textsubscript{3}Br</td>
<td>4.43 ± 0.02</td>
</tr>
<tr>
<td>H–CH\textsubscript{2}F\textsuperscript{2+}</td>
<td>0.4 ± 0.3</td>
<td>≤(0.1 ± 0.1)</td>
<td>H–CH\textsubscript{2}F\textsubscript{2}</td>
<td>4.48 ± 0.04</td>
</tr>
<tr>
<td>H–CH\textsubscript{2}Cl\textsuperscript{2+}</td>
<td>1.1 ± 0.4</td>
<td>≤(0.9 ± 0.2)</td>
<td>H–CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>4.15 ± 0.02</td>
</tr>
<tr>
<td>H–CH\textsubscript{3}\textsuperscript{3+}</td>
<td>–0.1 ± 0.4</td>
<td>≤(−0.2 ± 0.2)</td>
<td>H–CH\textsubscript{3}\textsuperscript{3}</td>
<td>4.61 ± 0.03</td>
</tr>
<tr>
<td>H–CC\textsubscript{3}Cl\textsuperscript{2+}</td>
<td>0.7 ± 0.3</td>
<td>≤(0.7 ± 0.3)</td>
<td>H–CC\textsubscript{3}Cl\textsubscript{2}</td>
<td>4.07 ± 0.03</td>
</tr>
<tr>
<td>F–CH\textsubscript{2}F\textsuperscript{+}</td>
<td>2.1 ± 0.3</td>
<td>≤(3.2 ± 0.1)</td>
<td>F–CH\textsubscript{2}F\textsubscript{2}</td>
<td>4.77 ± 0.09</td>
</tr>
<tr>
<td>F–CH\textsubscript{2}Cl\textsuperscript{+}</td>
<td>1.4 ± 0.2</td>
<td>≤(2.5 ± 0.1)</td>
<td>F–CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>5.14 ± 0.09</td>
</tr>
<tr>
<td>F–CH\textsubscript{2}Br\textsuperscript{+}</td>
<td>0.6 ± 0.3</td>
<td>≤(2.0 ± 0.4)</td>
<td>F–CH\textsubscript{2}Br\textsubscript{2}</td>
<td>5.53 ± 0.06</td>
</tr>
<tr>
<td>F–CH\textsubscript{2}I\textsuperscript{+}</td>
<td>1.5 ± 0.2</td>
<td>≤(3.9 ± 0.1)</td>
<td>F–CH\textsubscript{2}I\textsubscript{2}</td>
<td>5.00 ± 0.11</td>
</tr>
<tr>
<td>F–CF\textsubscript{3}Cl\textsuperscript{+}</td>
<td>1.2 ± 0.3</td>
<td>–\textsuperscript{e}</td>
<td>F–CF\textsubscript{3}Cl\textsubscript{2}</td>
<td>5.30</td>
</tr>
<tr>
<td>F–CF\textsubscript{3}Br\textsuperscript{+}</td>
<td>2.0 ± 0.3</td>
<td>–\textsuperscript{e}</td>
<td>F–CF\textsubscript{3}Br\textsubscript{2}</td>
<td>5.09\textsuperscript{b}</td>
</tr>
<tr>
<td>F–CF\textsubscript{3}I\textsuperscript{+}</td>
<td>2.7 ± 0.2\textsuperscript{g}</td>
<td>≤(2.7 ± 0.2)</td>
<td>F–CF\textsubscript{3}I\textsubscript{2}</td>
<td>5.40\textsuperscript{b}</td>
</tr>
<tr>
<td>F–CF\textsubscript{3}I\textsuperscript{+}</td>
<td>–0.7 ± 0.3</td>
<td>≤(1.0 ± 0.3)</td>
<td>F–CF\textsubscript{3}I\textsubscript{2}</td>
<td>5.67 ± 0.02</td>
</tr>
<tr>
<td>F–CC\textsubscript{3}Cl\textsuperscript{+}</td>
<td>0.9 ± 0.2</td>
<td>–\textsuperscript{e}</td>
<td>F–CC\textsubscript{3}Cl\textsubscript{2}</td>
<td>4.55 ± 0.04</td>
</tr>
</tbody>
</table>

(continued)
Table 11. Continued.

<table>
<thead>
<tr>
<th>Cation</th>
<th>$D_{\text{therm}}^{a+}$ (eV)</th>
<th>$D_{\text{expt}}^{a+}$ (eV)</th>
<th>Neutral</th>
<th>$D_{\text{lit}}^{c}$ (eV)</th>
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</thead>
<tbody>
<tr>
<td>F–SF$_5^+$</td>
<td>$-1.4 \pm 0.3$</td>
<td>$\leq (1.0 \pm 0.2)$</td>
<td>F–SF$_5$</td>
<td>4.06</td>
</tr>
<tr>
<td>F–SF$_4$Cl$^+$</td>
<td>$2.7 \pm 0.3$</td>
<td>$-^e$</td>
<td>F–SF$_4$Cl$^+$</td>
<td>3.70$^d$</td>
</tr>
<tr>
<td>F–SF$_4$CF$^+$</td>
<td>$-$</td>
<td>$-^e$</td>
<td>F–SF$_4$CF$_3$</td>
<td>$?^e$</td>
</tr>
<tr>
<td>F–C$_2$F$_5^+$</td>
<td>$5.7 \pm 0.2$</td>
<td>$\leq (6.5 \pm 0.1)$</td>
<td>F–C$_2$F$_3$</td>
<td>5.66 $\pm$ 0.13</td>
</tr>
<tr>
<td>F–C$_2$F$_3^+$</td>
<td>$1.5 \pm 0.3$</td>
<td>$\leq (3.4 \pm 0.2)$</td>
<td>F–C$_2$F$_3$</td>
<td>5.52 $\pm$ 0.07</td>
</tr>
<tr>
<td>F–C$_3$F$_3^+$</td>
<td>$2.6 \pm 0.3$</td>
<td>$\leq (3.5 \pm 0.3)$</td>
<td>F–C$_3$F$_3$</td>
<td>6.15</td>
</tr>
<tr>
<td>Cl–CH$_3^+$</td>
<td>$2.2 \pm 0.2$</td>
<td>$\leq (2.4 \pm 0.1)$</td>
<td>Cl–CH$_3$</td>
<td>3.63 $\pm$ 0.02</td>
</tr>
<tr>
<td>Cl–CH$_2$Cl$^+$</td>
<td>$0.9 \pm 0.2$</td>
<td>$\leq (1.6 \pm 0.1)$</td>
<td>Cl–CH$_2$Cl$^+$</td>
<td>3.50 $\pm$ 0.03</td>
</tr>
<tr>
<td>Cl–CHCl$_3^+$</td>
<td>$0.2 \pm 0.2$</td>
<td>$\leq (1.6 \pm 0.1)$</td>
<td>Cl–CHCl$_3$</td>
<td>3.22 $\pm$ 0.02</td>
</tr>
<tr>
<td>Cl–CFCl$_3^+$</td>
<td>$0.0 \pm 0.2$</td>
<td>$-^f$</td>
<td>Cl–CFCl$_2$</td>
<td>3.33 $\pm$ 0.09</td>
</tr>
<tr>
<td>Cl–CF$_2$Cl$^+$</td>
<td>$0.1 \pm 0.2$</td>
<td>$\leq (2.2 \pm 0.1)$</td>
<td>Cl–CF$_2$Cl$^+$</td>
<td>3.46 $\pm$ 0.11</td>
</tr>
<tr>
<td>Cl–CF$_3^+$</td>
<td>$0.4 \pm 0.3$</td>
<td>$-^e$</td>
<td>Cl–CF$_3$</td>
<td>3.79 $\pm$ 0.04</td>
</tr>
<tr>
<td>Cl–CCI$_3^+$</td>
<td>$-0.4 \pm 0.2$</td>
<td>$-^f$</td>
<td>Cl–CCI$_3$</td>
<td>3.07</td>
</tr>
<tr>
<td>Cl–SF$_5^+$</td>
<td>$0.0 \pm 0.2$</td>
<td>$\leq (1.9 \pm 0.3)$</td>
<td>Cl–SF$_5$</td>
<td>2.54</td>
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<tr>
<td>Br–CH$_3^+$</td>
<td>$2.3 \pm 0.1$</td>
<td>$\leq (2.3 \pm 0.1)$</td>
<td>Br–CH$_3$</td>
<td>3.05 $\pm$ 0.02</td>
</tr>
<tr>
<td>Br–CF$_3^+$</td>
<td>$0.6 \pm 0.1$</td>
<td>$-^e$</td>
<td>Br–CF$_3$</td>
<td>3.07 $\pm$ 0.01</td>
</tr>
<tr>
<td>I–CF$_1^+$</td>
<td>$1.0 \pm 0.1$</td>
<td>$\leq (1.5 \pm 0.2)$</td>
<td>I–CF$_5$</td>
<td>2.35 $\pm$ 0.01</td>
</tr>
<tr>
<td>H$_2$FC–H$^+$</td>
<td>$5.4 \pm 0.2$</td>
<td>$\leq (5.9 \pm 0.3)$</td>
<td>H$<em>2$FC–H$</em>^-$</td>
<td>4.39 $\pm$ 0.04</td>
</tr>
<tr>
<td>H$_2$Cl–H$^+$</td>
<td>$6.7 \pm 0.2$</td>
<td>$\leq (6.6 \pm 0.3)$</td>
<td>H$<em>2$Cl–H$</em>^-$</td>
<td>4.34 $\pm$ 0.02</td>
</tr>
<tr>
<td>H$_2$Br–H$^+$</td>
<td>$7.5 \pm 0.2$</td>
<td>$\leq (7.3 \pm 0.3)$</td>
<td>H$<em>2$Br–H$</em>^-$</td>
<td>4.43 $\pm$ 0.02</td>
</tr>
<tr>
<td>F$_3$C–H$^+$</td>
<td>$4.5 \pm 0.1$</td>
<td>$\leq (4.6 \pm 0.3)$</td>
<td>F$<em>3$C–H$</em>^-$</td>
<td>4.61 $\pm$ 0.03</td>
</tr>
<tr>
<td>F$_3$C–Cl$^+$</td>
<td>$4.4 \pm 0.1$</td>
<td>$\leq (4.9 \pm 0.3)$</td>
<td>F$<em>3$C–Cl$</em>^-$</td>
<td>3.79 $\pm$ 0.04</td>
</tr>
<tr>
<td>F$_3$C–Br$^+$</td>
<td>$3.4 \pm 0.1$</td>
<td>$\leq (3.9 \pm 0.3)$</td>
<td>F$<em>3$C–Br$</em>^-$</td>
<td>3.07 $\pm$ 0.01</td>
</tr>
<tr>
<td>F$_3$I$^+$</td>
<td>$2.4 \pm 0.1$</td>
<td>$\leq (2.4 \pm 0.3)$</td>
<td>F$<em>3$I$</em>^-$</td>
<td>2.35 $\pm$ 0.01</td>
</tr>
<tr>
<td>F$_5$S–F$^+$</td>
<td>$6.3 \pm 0.3$</td>
<td>$-^f$</td>
<td>F$<em>5$S–F$</em>^-$</td>
<td>4.06</td>
</tr>
<tr>
<td>F$_5$S–CF$_3^+$</td>
<td>$-0.4 \pm 0.4$</td>
<td>$-^f$</td>
<td>F$_5$S–CF$_3$</td>
<td>3.86 $\pm$ 0.45$^k$</td>
</tr>
<tr>
<td>F$_5$S–Cl$^+$</td>
<td>$3.0 \pm 0.3$</td>
<td>$-^f$</td>
<td>F$<em>5$S–Cl$</em>^-$</td>
<td>2.54$^d$</td>
</tr>
</tbody>
</table>

Notes: $^a$Thermochemical ionic bond dissociation energy at 298 K ($D_{\text{therm}}^{a+}$) for the bond shown in the first column. This value is calculated from the equation $D_{\text{therm}}^{a+} = \Delta_h H_{298}^0 - IE(ABC) + EA(A)$, where $\Delta_h H_{298}^0$ is the enthalpy change for the reaction $ABC \rightarrow A^+ + BC^+$, $IE$ is an ionisation energy and $EA$ an electron affinity.

$^b$Experimental ionic bond dissociation energy at 298 K ($D_{\text{expt}}^{a+}$) for the bond shown in the first column. This value is calculated from $D_{\text{expt}}^{a+} = AE(A) - IE(ABC) + EA(A)$, where $AE$ is the appearance energy of $A^-$ detected from the reaction $ABC \rightarrow A^- + BC^+$, $IE$ is an ionisation energy and $EA$ an electron affinity.

$^c$Neutral bond dissociation energy at 298 K for the bond shown in the fourth column from reference [64].

$^d$Experimental data not available because an accurate value for $AE(H^-)$ could not be obtained in either case due to the zero-blast effect [35].

$^e$Experimental data not available because ion-pair formation involves production of a neutral species in addition to the anion–cation pair.

$^f$Experimental data not available because production of the the anion is probably dominated by dissociative electron attachment, and not by ion-pair formation.

$^g$Assumes F$^-$ turns on at the thermochemical threshold for CF$_3$I $\rightarrow$ F$^-$ + CF$_3$I$^+$ (see Section 7).

$^h$Not quoted in reference [64]. Calculated from $\Delta_h H_{298}^0$ for the neutral dissociation reaction $ABC \rightarrow A + BC$. Data for $\Delta_h H_{298}^0$ of CF$_3$Br and CF$_3$I radicals are indirect values taken from references [94,95].

$^i$Not quoted in reference [64]. Calculated from $\Delta_h H_{298}^0$ for the neutral dissociation reaction $ABC \rightarrow A + BC$. Data for $\Delta_h H_{298}^0$ of SF$_4$Cl and SF$_5$ radicals are taken from reference [69].

$^j$Value at 0 K [56].
(b) In molecules containing both hydrogen and halogen atoms, quantum yields for the production of the atomic halogen anion are greater than for production of H\(^-\) anions. Note, however, that when the H\(^-\) signal was similar to or weaker than that of the halogen anion, it was not possible to determine absolute cross-sections and quantum yields for H\(^-\) formation due to the zero-blast effect (footnotes p and q in Table 10).

(c) For the fluoromethane series of molecules, the quantum yield at \(E_{\text{max}}\) for F\(^-\) formation decreases as the number of fluorine atoms increases: \(\Phi (\text{F}^-\text{ from CH}_3\text{F}) > \Phi (\text{F}^-\text{ from CH}_2\text{F}_2) > \Phi (\text{F}^-\text{ from CHF}_3) > \Phi (\text{F}^-\text{ from CF}_4)\). The opposite trend is observed for F\(^-\) anions produced from the chlorofluoromethanes: \(\Phi (\text{F}^-\text{ from CFCl}_3) < \Phi (\text{F}^-\text{ from CF}_2\text{Cl}_2) < \Phi (\text{F}^-\text{ from CF}_3\text{Cl})\).

(d) For the chloromethane series of molecules, the quantum yield at \(E_{\text{max}}\) for Cl\(^-\) formation also decreases as the number of chlorine atoms increases: \(\Phi (\text{Cl}^-\text{ from CH}_3\text{Cl}) > \Phi (\text{Cl}^-\text{ from CH}_2\text{Cl}_2) > \Phi (\text{Cl}^-\text{ from CHCl}_3)\). Again, the opposite trend is observed for Cl\(^-\) anions produced from the chlorofluoromethanes: \(\Phi (\text{Cl}^-\text{ from CF}_3\text{Cl}) < \Phi (\text{Cl}^-\text{ from CF}_2\text{Cl}_2)\). Note that the Cl\(^-\) signal observed from CFCl\(_3\) and CCl\(_4\) is dominated by dissociative electron attachment, and the contribution to its signal from ion-pair formation is not known.

(e) For the hydrocarbon series of molecules, the quantum yield at \(E_{\text{max}}\) for H\(^-\) formation increases as the number of hydrogen atoms increases: \(\Phi (\text{H}^-\text{ from CH}_4) < \Phi (\text{H}^-\text{ from C}_2\text{H}_4) < \Phi (\text{H}^-\text{ from C}_2\text{H}_6) < \Phi (\text{H}^-\text{ from C}_3\text{H}_8)\). It is noted that the value for H\(^-\) from CH\(_4\), \(4.4 \times 10^{-6}\), is based on our value of \(1.4 \times 10^{-22}\) cm\(^2\) for the cross-section for H\(^-\) formation at 20.6 eV [19]. This is a factor of ca. 70 smaller than the value of the cross-section quoted by Mitsuke et al. [7]. It is not clear what normalisation and correction factors have been applied to the signals by Mitsuke et al., and in particular whether any mass discrimination correction for detection of m/z 1 anions in their quadrupole spectrometer has been made. Since our values for H\(^-\) from C\(_2\)H\(_6\) and C\(_3\)H\(_8\) are in much closer agreement, it does not appear that the detection of m/z 1 anions is the reason, per se, for the anomalously high value of Mitsuke et al. for the cross-section for H\(^-\) production from CH\(_4\).

(f) In comparing fully hydrogenated and fully fluorinated molecules (e.g. CH\(_4\) vs. CF\(_4\), C\(_3\)H\(_8\) vs. C\(_3\)F\(_8\)), the maximum cross-section for F\(^-\) production always exceeds that for H\(^-\) production. Thus for the molecules CH(F)\(_4\), C\(_2\)H(F)\(_4\), C\(_2\)H(F)\(_6\) and C\(_3\)H(F)\(_8\), in each case, in the range 10–25 eV the maximum value of \(\sigma (\text{F}^-)\) is a factor of 2–18 times greater than the corresponding value for H\(^-\) formation.

These statements may be understood better if one considers the electronegativity of the individual atoms, and therefore the overall polarisation of the electron density across the molecule. Pauling electronegativities for the relevant atoms are: F (3.98), Cl (3.16), Br (2.96), I (2.66), S (2.58), C (2.55) and H (2.20) [116]. For example, the bond polarisation in CH\(_4\) can be represented by C\(^3-\)–H\(^6+\), but in CF\(_4\) by C\(^3+\)–F\(^-\). The effects of fluorine substitution on the four hydrogen atoms in methane have been studied by Brundle et al. [107], where they calculate that in moving from CH\(_4\) through the three hydrofluoromethanes to CF\(_4\), the carbon atom surrenders over 1.6 electrons to the fluorines, mostly through polarisation of the C–X bonds. Qualitatively, therefore, one can explain point (f) above and appreciate that F\(^-\) formation from CF\(_4\) might be more probable than H\(^-\)
from CH$_4$. We can also consider the experimental data in point (c) for the fluoromethanes. Although the carbon atom gives up more charge as H atoms are substituted for F atoms in CF$_4$, the electron density on any one given F atom will be reduced when the total number of F atoms within the molecule increases. The same argument can be followed to explain the experimental data in (d) for the chloromethanes. For any chlorofluoromethane, however, the central carbon is always bonded to four highly electronegative species – the difference between electronegativities for F and Cl is relatively small. Now perhaps a statistical factor plays a part, whereby the number of F or Cl atoms determines which anion is formed in preference to the other; indeed the quantum yields at $E(\sigma_{\text{max}})$ for F$^-$ and Cl$^-$ from CF$_2$Cl$_2$ are almost identical (Table 10).

It is incorrect, however, to attempt to understand any of the above statements by considering absolute energetic quantities such as electron affinities or bond dissociation energies; these values simply determine the asymptotic dissociation energy for the ion-pair state. It is also incorrect to assume that the polarity of the breaking bond is the sole factor to determine the relative quantum yields of atomic anions. This effect may contribute, but is probably not the dominant factor. All the evidence for the molecules studied in detail (Section 6) is that, assuming indirect formation of ion pairs via an excited neutral state, it is the dynamics of the crossing between the Rydberg and ion-pair states which is the most important factor, and indeed the probability for the excited state to decay by a different process. Therefore, the position of the ion-pair state along the reaction coordinate (i.e. the value for its equilibrium bond separation, $r_e$) and its shape are significant.

### 8.4. Competing ion-pair reactions

It is observed from many of these ion-pair studies that different anions from the same molecule display peaks in their ion yields at the same energy. These peaks most likely identify the same excited intermediate state, and this is further evidence that ion pairs are commonly formed by an indirect mechanism. Specific examples for CH$_2$F$_2$ and CF$_3$Cl are discussed below.

The spectra for anions produced from CH$_2$F$_2$ are shown in Figure 26. The first band in the H$^-$ spectrum shows vibrational structure consistent with that observed by photoelectron spectroscopy for the ground state of CH$_2$F$_2^+$, $X^2B_2$ [63,99]. The peaks in this band are assigned using the Rydberg formula to overlapping members of the 5$p$ and 6$p$$^1B_2$ Rydberg series. The band at 12.56 eV most likely corresponds to the maximum of the vibrational distribution of the 5$p$ Rydberg series. The bands at 12.69, 12.82, 12.94, 13.07 and 13.20 eV correspond to vibrationally resolved components of the 6$p$ Rydberg series with a quantum defect of ca. 0.55–0.65 [117]. It is clear that two different ion-pair dissociation channels are competing following excitation to the 5$p$ Rydberg state, CH$_2$F$_2^+ \rightarrow$ F$^-+CH_2F^+$ and CH$_2$F$_2^+ \rightarrow$ H$^-+CHF^+$. However, the F$^-$ channel no longer competes following excitation to higher vibrational members of the 6$p$ Rydberg state; the first peak in the F$^-$ spectrum spans 11.8 to 13.1 eV only. The 6$p$ Rydberg state overlaps with the ground state of CH$_2$F$_2^+$, $X^2B_2$; the adiabatic IE is 12.726 eV and the vertical IE is 13.141 eV [63]. Furthermore at 13.06 eV, CH$_2$F$_2^+$ becomes unstable with respect to H$^-$+CHF$_2^+$ [63]. This dissociation is therefore complementary to the CH$_2$F$_2^+ \rightarrow$ H$^-+CHF^+$ ion-pair dissociation, but not to CH$_2$F$_2^+ \rightarrow$ F$^-+CH_2F^+$. This may explain why the F$^-$ dissociation channel diminishes at
13.1 eV, while that for H\textsuperscript{−} continues. Although an absolute cross-section for H\textsuperscript{−} formation was not determined due to the zero-blast effect, its signal strength at ca. 12.6 eV is slightly weaker than but comparable to that of the F\textsuperscript{−} signal. The F\textsuperscript{−} cross-section at this energy is ca. 5 × 10\textsuperscript{−21 cm\textsuperscript{2}}.

Ion-pair formation from CF\textsubscript{3}Cl was discussed in detail in Section 6.2. The F\textsuperscript{−} and Cl\textsuperscript{−} spectra (Figures 13 and 14) share some common features, and the two spectra are compared directly in Figure 34. F\textsuperscript{−} and Cl\textsuperscript{−} anions were both detected at 17.6 eV, but only the Cl\textsuperscript{−} ion yield displays a resolved peak at this energy. The range from 16–18 eV is the only region across the two spectra where the Cl\textsuperscript{−} cross-section exceeds that for F\textsuperscript{−}. The two spectra cross at 18.4 eV and 28.2 eV, and between these energies the F\textsuperscript{−} cross-section is significantly larger than that for Cl\textsuperscript{−}. The fact that features are observed in both spectra at similar energies suggests that these do indeed represent competing decay channels from the same Rydberg states. Vertical ionisation energies for CF\textsubscript{3}Cl\textsuperscript{+} D\textsuperscript{2} E, E\textsuperscript{2} A\textsubscript{1}, F\textsuperscript{2} E and G\textsuperscript{2} A\textsubscript{1} are 17.71, 20.20, 21.20 and 23.80 eV, respectively [77,118]. The features in the Cl\textsuperscript{−} spectrum at 17.6, 19.7 and 20.9 eV are assigned to high-lying Rydberg states (n > 5) converging on the D, E and F ionisation limits, respectively. The shoulder at 22.5 eV is assigned as either the 3\textit{p} \textsuperscript{1} A\textsubscript{1} or 4\textit{s} \textsuperscript{1} A\textsubscript{1} Rydberg state converging on the G ionisation limit.

Section 8.3 addressed general trends in quantum yield and cross-section values, only comparing those in Table 10 quoted at \(E_{\text{max}}\). The data for F\textsuperscript{−} and Cl\textsuperscript{−} from CF\textsubscript{3}Cl, however, is one example showing that cross-section and quantum yield values should be compared at the same energy; in this particular case, the values for F\textsuperscript{−} are a factor of ca. 6 greater than for Cl\textsuperscript{−} production at an energy of 21.0 eV. This point is perhaps obvious, but it serves to highlight the challenges in understanding why one particular anion has a higher probability for formation than another.

### 8.5. Anions formed by dissociative electron attachment

For a molecule under study by negative photoion spectroscopy, below the IE any anion produced can only result from an ion-pair reaction. Above the IE, however, photoelectrons are simultaneously produced, and negative ions can also result from an electron attachment process. Examples where this has been observed include: SF\textsubscript{5}\textsuperscript{−} and SF\textsubscript{6}\textsuperscript{−} from SF\textsubscript{6}, SF\textsubscript{5}\textsuperscript{−} from SF\textsubscript{2}CF\textsubscript{3} (Sections 5.1 and 5.3); Br\textsuperscript{−} from CF\textsubscript{3}Br and I\textsuperscript{−} from CF\textsubscript{3}I (Section 6.2); SF\textsubscript{5}\textsuperscript{−} from SF\textsubscript{2}Cl (Section 6.1); Cl\textsuperscript{−} from CFC\textsubscript{1}\textsubscript{3} and Cl\textsuperscript{−} from CCl\textsubscript{4} (Table 10, Figures 30 and 32). The electron attachment process for the generic polyatomic molecule ABC can be described by

\[
ABC + hv \rightarrow ABC^+ + e^− \tag{39}
\]

\[
ABC + e^− \rightarrow ABC^- \quad \text{or} \quad A^- + BC \quad \text{or} \quad A^- + B + C. \tag{40}
\]

Four points are made when identifying such electron attachment processes:

1. A plot of the anion signal as a function of gas pressure will be linear for ion-pair formation, but non-linear (with the rate of change in signal increasing with increasing pressure) if electron attachment is dominant. Figure 5 shows examples for F\textsuperscript{−} and SF\textsubscript{5}\textsuperscript{−} from SF\textsubscript{6}. Following reactions (39) and (40), a quadratic dependence of the signal of A\textsuperscript{−} with pressure of ABC is to be expected.
ABC must have an electron attachment rate coefficient, $k_a$, of sufficient magnitude for this process to be observed at a rate comparable with ion-pair formation. Not surprisingly, the molecules listed above all have very fast thermal $k_a$ values, lying between $1 \times 10^{-8}$ and $4 \times 10^{-7}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (footnote u in Table 10). Molecules with slightly lower $k_a$ values were also studied (e.g. CHCl$_3$ and CF$_2$Cl$_2$ ($k_a = 4.7 \times 10^{-9}$ and $1.9 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively) [119]), but the anion signals were all attributed to ion-pair formation since they showed a linear dependence with pressure. It appears that there is a threshold rate coefficient of ca. $5 \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, below which the value is too slow for anions to form effectively by dissociative electron attachment.

(3) There is usually only one anion produced by electron attachment from any given molecule which is detected by negative photoion spectroscopy (the exception being...
SF$_6^-$ and SF$_5^-$ being formed from SF$_6$). This anion always matches the dominant species identified from independent thermal electron attachment experiments in which the mass of the product anion is detected.

(4) The spectrum of an anion produced by electron attachment matches, to varying extent depending on the molecule and signal strength, the TPES for that molecule. In most cases peak positions are the same, but relative intensities of peaks can vary significantly.

The most interesting point is probably the final one. The similarities/differences between an anion spectrum produced predominantly by electron attachment and the molecular TPES have already been mentioned for the molecules SF$_6$, SF$_2$CF$_3$, CF$_3$Br, CF$_3$I and SF$_5$Cl in Sections 5 and 6, and in detail in the original papers [17,18,21]. Taking SF$_6$ as the example where there is the closest similarity between the SF$_6^-$ yield and the TPES of SF$_6$ (Figure 4), the only significant difference between the two spectra is the peak at 19.9 eV which appears ca. two times more intense in the SF$_6^-$ spectrum. The same point about the intensity of this peak has been discussed by Yencha et al. [40] who compared their TPES of SF$_6$ with the ion yield of SF$_6^-$ from SF$_6$ reported by Mitsuke et al. [9]. The $k_a$ value for this molecule is high, $2.4 \times 10^{-7}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. The angular momentum of the attaching electron is composed of linear combinations of components with quantum numbers $l=0$ (s wave), $l=1$ (p wave), $l=2$ (d wave) etc. The cross-section for non-dissociative electron attachment to SF$_6$ peaks at very low energy which is a characteristic of s-wave capture [47], but SF$_6^-$ anions observed from reaction (8) will arise from all electrons integrated under the cross-section versus electron energy distribution. By contrast, the TPES arises only from low-energy electrons detected within the bandpass of the threshold analyser, ca. 4 meV in the experiment of Yencha et al. [40]. In practice, the experimentally observed resolution will depend upon a convolution of the electron energy distribution and the resolution of the photon source. In both experiments the monochromator resolution, ca. 0.4 nm or 130 meV at 19.9 eV, will probably dominate. Notwithstanding this point, there is no reason why the intensities of the TPES and SF$_6^-$ spectra in Figure 4 should be exactly the same, and this may explain the small differences that have been observed both by us and by Yencha et al. We also note that this difference is not be a particular property of SF$_6$, because a greater inconsistency in intensities in the threshold photoelectron and parent anion yields has been observed with another polyatomic molecule which attaches electron very rapidly, cyclic-C$_5$F$_8$ [120], with a $k_a$ value, $3.6 \times 10^{-7}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, similar to that of SF$_6$ [121]. We should also note that the yield of SF$_5^-$ also show many similarities to the TPES of SF$_6$. The enthalpy change for the reaction SF$_6$ + $h\nu$ → SF$_5^-$ + F$^+$ is 17.6 eV. Below this energy, therefore, SF$_5^-$ can only form by dissociative electron attachment. Above this energy, there exists the possibility that a small amount of SF$_5^-$ is produced via this ion-pair reaction.

Comparing all the molecules in which an anion is produced predominantly by electron attachment, there is unfortunately no general trend whether the ‘agreement’, however that is quantified, between the two spectra correlates with any physical property, such as the $k_a$ value. As highlighted above for SF$_6$ and c-C$_5$F$_8$, the reasons for any differences cannot be easily explained. New data for Cl$^-$ from CFCl$_3$ and CCl$_4$ are shown in Figures 32 and 30, respectively, and Table 10. Both spectra show a remarkable tendency for the relative anion signal to increase with increasing photon energy, especially above ca. 22 eV; this is seen most clearly in comparing the Cl$^-$ ion yield from CCl$_4$ with the TPES of this
molecule (Figure 30). It is even possible that some of the features observed above 22 eV identify inner-valence-shell ionisation energies which are very weak or absent in the TPES. Furthermore, Cl$^-$ signal versus pressure plots recorded at these peak energies continue to maintain a non-linear dependence with pressure, as discussed in point (1) above. For the Cl$^-$ from CCl$_4$ example, a close examination of the TPES does indeed reveal weak and partially resolved features between 24 and 30 eV.

9. Conclusions

The formation of ion pairs from polyatomic molecules is a weak process; quantum yields are typically less than ca. $10^{-3}$ or 0.1%. The detection of ion-pair formation therefore requires a sensitive experimental apparatus, and most spectra could only be recorded at a relatively modest resolution of ca. 0.1–0.6 nm. Ion-pair formation is most commonly formed by an indirect mechanism via an initially excited Rydberg state of the parent molecule. Many peaks in ion-pair spectra occur between adiabatic and vertical ionisation energy values of either the ground or an excited electronic state of the parent cation. Indeed, many of the strongest anion signals result following predissociation of high-lying Rydberg states ($n > 5$). It can be difficult to resolve these overlapping excited states, let alone assign them, especially when the resolution of the experiment is limited.

One of the most interesting questions raised is: why is one anion produced preferentially to another? This question can be asked when comparing the same anion from different molecules (e.g. Cl$^-$ from CF$_3$Cl and CF$_3$Cl$_2$), different anions from different molecules (e.g. H$^-$ from CH$_4$ and F$^-$ from CF$_4$) and different anions from the same molecule (e.g. F$^-$ and Cl$^-$ from CF$_3$Cl). Some trends are apparent when comparing a series of similar molecules (e.g. the methyl halides, the fluoromethanes or the chloromethanes (Section 8.3)), but there is no common explanation. Another unanswered question is: why are some anions not observed at all? Examples include the absence of Cl$^-$ anions from CF$_3$Cl below 16 eV via the reaction CF$_3$Cl $\rightarrow$ Cl$^- +$ CF$_3$ (Section 6.2), and the complete absence of Cl$^-$ anions from SF$_5$Cl above 12 eV (Section 6.1).

Thermochemistry is a useful tool to identify the cation and neutral dissociation fragments accompanying the detected anion. However, conclusive assignments can only realistically be made at the onset for ion-pair formation when one unique dissociation reaction is energetically allowed. The ideal experiment would detect anion and cation fragments above the ionisation energy in coincidence, and perhaps this is where the future of ion-pair spectroscopy lies. Such coincidence experiments would identify both the anion and cation fragments [122], allowing for a more detailed analysis of ion-pair dissociation dynamics. Finally, it is noted that there is very little information known about ion-pair potential energy surfaces in polyatomic molecules, and the dynamics of dissociation from these surfaces. For example, one might be able to use Equation (IV) to model the potential energy function of an ion-pair state if constants $A$ and $\alpha$ can be derived from experimental results. It is to be hoped that the vast amount of experimental data presented in this review will stimulate interest in theoreticians to tackle such problems.
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Note

The ion yield of Cl$^-$ from CHCl$_3$ between 10–20 eV has very recently been published on the web (Chen et al., J. Phys. Chem A, DOI: 10.1021/jp2000927). No other anions are reported. The Cl$^-$ spectrum shows its maximum signal at ca. 12 eV. The spectrum appears to show little relation to that observed by us (Figure 29 of this review).

References