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## Vacuum-UV negative photoion spectroscopy of SF<sub>5</sub>CF<sub>3</sub>

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Ion pair formation, generically described as  $AB \rightarrow A^+ + B^-$ , from vacuum-UV photoexcitation of trifluoromethyl sulfur pentafluoride, SF<sub>5</sub>CF<sub>3</sub>, has been studied by anion mass spectrometry using synchrotron radiation in the photon energy range of 10–35 eV. The anions F<sup>-</sup>, F<sub>2</sub><sup>-</sup>, and SF<sub>x</sub><sup>-</sup> ( $x=1-5$ ) are observed. With the exception of SF<sub>5</sub><sup>-</sup>, the anions observed show a linear dependence of signal with pressure, showing that they arise from ion pair formation. SF<sub>5</sub><sup>-</sup> arises from dissociative electron attachment, following photoionization of SF<sub>5</sub>CF<sub>3</sub> as the source of low-energy electrons. Cross sections for anion production are put on to an absolute scale by calibration of the signal strengths with those of F<sup>-</sup> from both SF<sub>6</sub> and CF<sub>4</sub>. Quantum yields for anion production from SF<sub>5</sub>CF<sub>3</sub>, spanning the range of 10<sup>-7</sup>–10<sup>-4</sup>, are obtained using vacuum-UV absorption cross sections. Unlike SF<sub>6</sub> and CF<sub>4</sub>, the quantum yield for F<sup>-</sup> production from SF<sub>5</sub>CF<sub>3</sub> increases above the onset of photoionization. © 2008 American Institute of Physics. [DOI: 10.1063/1.2894869]

### I. INTRODUCTION

The presence of the super greenhouse gas trifluoromethyl sulfur pentafluoride, SF<sub>5</sub>CF<sub>3</sub>, in the atmosphere was first reported in 2000 by Sturges *et al.*<sup>1</sup> Although the known atmospheric concentrations of SF<sub>5</sub>CF<sub>3</sub> are very low, its lifetime is in the region of 1000 years,<sup>2</sup> and it is thought to have a global warming potential 18 000 times greater than CO<sub>2</sub>, absorbing strongly in the infrared between 750 and 1250 cm<sup>-1</sup> (Ref. 3). Of anthropogenic origin, SF<sub>5</sub>CF<sub>3</sub> has been linked to SF<sub>6</sub> production and the manufacture of fluorochemicals,<sup>1</sup> but in truth the main source of this potent greenhouse gas has not yet unambiguously been identified. Since its discovery, SF<sub>5</sub>CF<sub>3</sub> has been the focus of numerous studies aimed to better understand its spectroscopic properties and reactivity. Laboratory experiments have confirmed the original estimates on the severity of SF<sub>5</sub>CF<sub>3</sub> as a greenhouse gas,<sup>3-6</sup> yet more work is required to gather a more comprehensive understanding of its sources and sinks. The original suggestion that SF<sub>5</sub> and CF<sub>3</sub> radicals combine to produce SF<sub>5</sub>CF<sub>3</sub> in high voltage equipment<sup>1</sup> has since been disputed;<sup>7</sup> reactions mimicking these conditions showed no evidence of SF<sub>5</sub>CF<sub>3</sub> production, although small amounts were detected when SF<sub>6</sub> reacted with some hydrofluorocarbons in a spark discharge.<sup>7</sup> Low-energy electron attachment to SF<sub>5</sub>CF<sub>3</sub> is dissociative<sup>8-12</sup> and may provide a mechanism for atmospheric removal, but stratospheric UV photolysis is unlikely to contribute due to the absence of photoabsorption by SF<sub>5</sub>CF<sub>3</sub> below 8 eV (Ref. 4) and the high value of the SF<sub>5</sub>-CF<sub>3</sub> bond dissociation energy (4.06 ± 0.45 eV at 0 K).<sup>13,14</sup> Following a new measurement of the ionization energy of the CF<sub>3</sub> radical,<sup>15</sup> this bond strength has since been refined to 3.86 ± 0.45 eV.<sup>16</sup>

The surprisingly high value of the S-C bond strength has spurred investigations into the sink routes for SF<sub>5</sub>CF<sub>3</sub> that might occur at higher altitudes in the mesosphere or ionosphere: Ion-molecule reactions, electron attachment, and vacuum-UV (VUV) photodissociation at the Lyman- $\alpha$  wavelength of 121.6 nm. Ion-molecule reaction studies have shown that both cations<sup>17,18</sup> and anions<sup>19</sup> react rapidly with SF<sub>5</sub>CF<sub>3</sub> and may therefore remove it from the mesosphere/ionosphere. However, the concentration of atmospherically relevant ions (e.g., O<sup>+</sup>, O<sub>2</sub><sup>+</sup>, N<sup>+</sup>, N<sub>2</sub><sup>+</sup>) is so low that the pseudo-first-order rate constant for ion-molecule reactions,  $\Sigma k_{\text{ion}}[\text{ion}]$ , is too small for this channel to contribute to any significant extent.<sup>16</sup> Low-energy electron attachment to SF<sub>5</sub>CF<sub>3</sub> is relatively fast,  $7.7 \times 10^{-8}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K,<sup>8</sup> and the absorption cross section at 121.6 nm is surprisingly high, approximately 10<sup>-17</sup> cm<sup>2</sup> (Refs. 2 and 20). By comparison with equivalent data for SF<sub>6</sub>, it was shown that the electron attachment process is responsible for ~99% of the removal of SF<sub>5</sub>CF<sub>3</sub> in the mesosphere, VUV photodissociation ~1%.<sup>2</sup> However, the long lifetime of SF<sub>5</sub>CF<sub>3</sub> in the earth's atmosphere, ~1000 years, is not determined by these *microscopic* chemical processes that occur in the mesosphere, but by the much slower *macroscopic* meteorology that transports the pollutant from the earth's surface up into the mesosphere.<sup>2</sup> Advances made in the last six years to understand the chemical physics properties and environmental impact of SF<sub>5</sub>CF<sub>3</sub> since its discovery in 2000 have been reviewed.<sup>16</sup>

One of the possible products following VUV photoexcitation of SF<sub>5</sub>CF<sub>3</sub> at 121.6 nm is ion-pair formation, e.g., CF<sub>3</sub><sup>+</sup>+SF<sub>5</sub><sup>-</sup> (Ref. 2). In this paper we describe an experiment to detect anions following VUV excitation as a means to study the dynamics of electronically excited states of SF<sub>5</sub>CF<sub>3</sub>. Absolute cross sections for anion production and, using photoabsorption data,<sup>20</sup> quantum yields have been evaluated for all the anion products observed. Photoion pair

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formation has been observed from many diatomic and small polyatomic molecules since the 1930s.<sup>21</sup> Ion pair states are reached either by direct photoabsorption or via predissociation following photoexcitation to an excited electronic state (which is usually Rydberg in character).<sup>21,22</sup> Based on Frank–Condon arguments, the latter process is thought to be more common, although significant coupling between Rydberg and ion pair states is a requirement—one which is not always met. The study of ion pair formation, therefore, can provide insight into the initial processes involved before the positive-negative pair of ions evolves, i.e., the decay dynamics of Rydberg states. Above the ionization energy (IE) of the parent neutral molecule, photoionization dominates and quantum yields for ion pair formation,  $\Phi_{\text{IP}}$ , are expected to be low, typically less than  $10^{-3}$ . Even below the IE, for polyatomic molecules  $\Phi_{\text{IP}}$  is typically only  $\sim 10^{-2}$  (Ref. 22). A recent ion pair study on  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CF}_2\text{Cl}_2$ , studying specifically the photon energy region below the IE of the parent neutral, has highlighted the significance of predissociation into a state yielding neutral fragments rather than one yielding ion pairs.<sup>23</sup> In addition to  $\text{SF}_5\text{CF}_3$ , the closely related molecules  $\text{SF}_6$  and  $\text{CF}_4$  have also been investigated in this paper. The photoion pair formation of  $\text{SF}_6$  into  $\text{SF}_5^+ + \text{F}^-$  and  $\text{CF}_4$  into  $\text{CF}_3^+ + \text{F}^-$  has been studied previously by Mitsuke *et al.*<sup>24,25</sup> and Scully *et al.*<sup>26</sup> We have seen a much larger number of anions than observed by these groups, and the data of Mitsuke *et al.*<sup>24,25</sup> have allowed us to put our  $\text{SF}_5\text{CF}_3$  data on an *absolute* scale. To our knowledge this is the first report of ion pair production following VUV photoexcitation of  $\text{SF}_5\text{CF}_3$ .

## II. EXPERIMENTAL

Beamline 3.1 at the UK Daresbury synchrotron radiation source (SRS) is optimized for high flux in the VUV,<sup>27</sup> and a 1 m Wadsworth monochromator provided the source of tunable radiation ( $\sim 8$ – $35$  eV) used for this experiment. The optimum resolution of this beamline is 0.05 nm, or 0.016 eV at 20 eV. A 2 mm diameter, 300 mm long capillary light guide connecting the experimental apparatus to the beamline focuses monochromatized light directly to the interaction region. The ion pair apparatus has been described in detail elsewhere.<sup>28</sup> Briefly, the gas under study is injected via a needle generating a directed jet which bisects orthogonally the incident photon beam. The crossing point, which dictates the center 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 toward a three-element electrostatic lens for focusing, 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 in which the monochromator is scanned are flux normalized using a sodium salicylate window and visible photomultiplier tube (EMI 9924B) 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 separately by turbopumps which are backed by a common rotary pump, and the base pressure of the apparatus is  $\sim 10^{-7}$  mbar. With sample gas running, the typical pressure in the chamber is  $\sim 10^{-5}$  mbar. The pressure inside the chamber was measured using an ionization gauge, the sensitivity of which to  $\text{SF}_6$ ,  $\text{CF}_4$ , and  $\text{SF}_5\text{CF}_3$  is calibrated in a separate experiment relative to  $\text{N}_2$  gas using a capacitance manometer.

Mass spectra are recorded to observe all anions produced from photoabsorption of the sample gas by exposure to white light, i.e., a wavelength of 0 nm. The mass-to-charge ratio ( $m/z$ ) of each peak in the mass spectrum is then fixed and the signal recorded as a function of sample gas pressure over the typical range of  $(0.5$ – $5.0) \times 10^{-5}$  mbar. Anions which show a nonlinear dependence with pressure cannot be assigned as ion pair products, and their signal is most likely influenced by secondary processes. Anions which show a linear dependence of signal with pressure can be attributed to ion pair formation. For all anions produced from  $\text{SF}_6$ ,  $\text{CF}_4$ , and  $\text{SF}_5\text{CF}_3$ , ion yields were recorded as a function of photon energy from 8–35 eV. Two gratings span this range, the higher-energy grating covering 12–35 eV. The majority of experiments were performed with this grating. The lower-energy grating covers the range of 8–18 eV, and for scans below 11.8 eV (or 105 nm) a LiF window can be inserted to eliminate higher-order radiation. This grating was used in one scan to record the threshold region of  $\text{F}^-$  from  $\text{SF}_5\text{CF}_3$ . Gas samples were obtained from Apollo Scientific with a quoted purity of  $>99.9\%$  and were used without further purification.

The ion yields are presented as anion cross sections  $\sigma$  in units of  $\text{cm}^2$ . The value of  $\sigma$  at photon energy  $h\nu$  is given by

$$\sigma(h\nu) = k \left( \frac{Sm}{frp} \right), \quad (1)$$

$S$  is the detected signal in counts  $\text{s}^{-1}$ ,  $f$  the relative photon flux,  $p$  the sample gas pressure adjusted for ionization gauge sensitivity,  $r$  the storage ring current,  $m$  the relative mass sensitivity of the quadrupole, and  $k$  a normalization constant. Thus the signal strength is normalized to photon flux, pressure, ring current, and mass sensitivity of the quadrupole. The relative photon flux as a function of  $h\nu$  is measured in a separate experiment with no sample gas present, so it is necessary to correct  $S$  both for  $f$  and  $r$ . The value of  $m$  as a function of mass in the range of 19–127 u (i.e.,  $\text{F}^-$  to  $\text{SF}_5^-$ ) is derived from a comparison of the cation spectrum produced by 70 eV electron impact ionization of the sample gas (with the photon beam blocked) with that published elsewhere.<sup>29</sup> Like most quadrupoles, the sensitivity of our mass spectrometer decreases with increasing mass of the ion;  $m$ , as defined in Eq. (1), therefore increases with increasing mass. The corrected signal for  $\text{F}^-$  from  $\text{SF}_6$  is then normalized to the known cross section at 14.3 eV,  $(7 \pm 2) \times 10^{-21} \text{ cm}^2$  (Ref. 24). Likewise, the corrected signal for  $\text{F}^-$  from  $\text{CF}_4$  is normalized to its value at 13.9 eV,  $(1.25 \pm 0.25) \times 10^{-21} \text{ cm}^2$  (Ref. 25). [It is noted that these cross section values are not strictly absolute, but are obtained from calibrated measurements of  $\text{O}^-$  yields from  $\text{O}_2$  (Ref. 30)]. In theory, the values  $k(\text{F}^-/\text{SF}_6)$  and  $k(\text{F}^-/\text{CF}_4)$  should

then be equal, but, in fact, they differ by a factor of 1.6. Given the number of corrections made to the anion signals, this difference seems a reasonable representation of experimental error. An average of the two  $k$  values is then used in Eq. (1) to determine absolute cross sections for the SF<sub>5</sub>CF<sub>3</sub> anion signals. We comment that, while these values of anion cross sections probably have an error as high as  $\pm 50\%$ – $100\%$ , such absolute measurements are notoriously difficult and prone to errors which are often underestimated in the literature. Scully *et al.*<sup>26</sup> estimated the cross section for the F<sup>−</sup> peak from SF<sub>6</sub> at 24.6 eV to be  $(2.0 \pm 0.5) \times 10^{-21}$  cm<sup>2</sup>, and this value agrees within experimental error with our value of  $1.6 \times 10^{-21}$  cm<sup>2</sup>. Likewise, Scully<sup>31</sup> estimated the cross section for F<sup>−</sup> production from CF<sub>4</sub> at 21.8 eV to be  $(5 \pm 1) \times 10^{-22}$  cm<sup>2</sup>, again agreeing reasonably well with our value of  $6.7 \times 10^{-22}$  cm<sup>2</sup>. This confirms that our method of determining absolute cross sections by normalizing the signal at one energy is applicable across the complete energy range of the experiment, approximately 10–25 eV. We believe it is therefore appropriate to present *all* the anion yields as absolute cross sections.

### III. THERMOCHEMISTRY: GENERAL COMMENTS

Our work also determines appearance energies (AEs) at 298 K for many fragment anions from SF<sub>5</sub>CF<sub>3</sub>, CF<sub>4</sub>, and SF<sub>6</sub>, and we compare these values with those calculated from thermochemical data. Berkowitz<sup>21</sup> has noted that, for many polyatomic molecules, a calculated threshold energy provided a lower limit to the experimental AE of an anion when suitable assumptions were made about the nature of the accompanying cation and/or neutral fragments. However, usually there was equality in these two values, although it is noted that *energy* and *enthalpy* are often indistinguishable words. In making comparisons between our experimental AE values of anions and calculated enthalpies of appropriate dissociation reactions, we make two assumptions which we believe are justified at the relatively modest resolution of our experiment, approximately 0.1–0.2 eV. First, it is now well established that it is not accurate to equate an AE<sub>298</sub> to the enthalpy of the corresponding unimolecular reaction at 298 K because of thermal effects.<sup>32</sup> In practice, the corrections needed to the AE<sub>298</sub> values are typically only 0.05–0.15 eV, and we feel justified in ignoring them. Second, the effects of entropy are disregarded in our calculations, even though many of the unimolecular reactions involve a value for  $\Delta n > 0$ , where  $\Delta n$  is the number of product species minus the number of reactant species. Thus  $\Delta_r S_{298}^0$  will be positive, and  $\Delta_r G_{298}^0$  for the unimolecular reactions will be more negative than the calculated  $\Delta_r H_{298}^0$  values. Finally, we should note that many of the values of enthalpies of formation,  $\Delta_f H_{298}^0$ , for polyatomic fragments from SF<sub>5</sub>CF<sub>3</sub> (e.g., SF<sub>4</sub>CF<sub>3</sub>, SF<sub>3</sub>CF<sub>3</sub><sup>+</sup>) are not known, and this places a severe limitation on the extent to which we can interpret the AE values for anions produced from SF<sub>5</sub>CF<sub>3</sub>. Even for SF<sub>6</sub>, there is still uncertainty in values for  $\Delta_r H_{298}^0$  of the SF<sub>*x*</sub><sup>(+)</sup> species ( $x=3-5$ ). Data for fragments of CF<sub>4</sub> are better established.

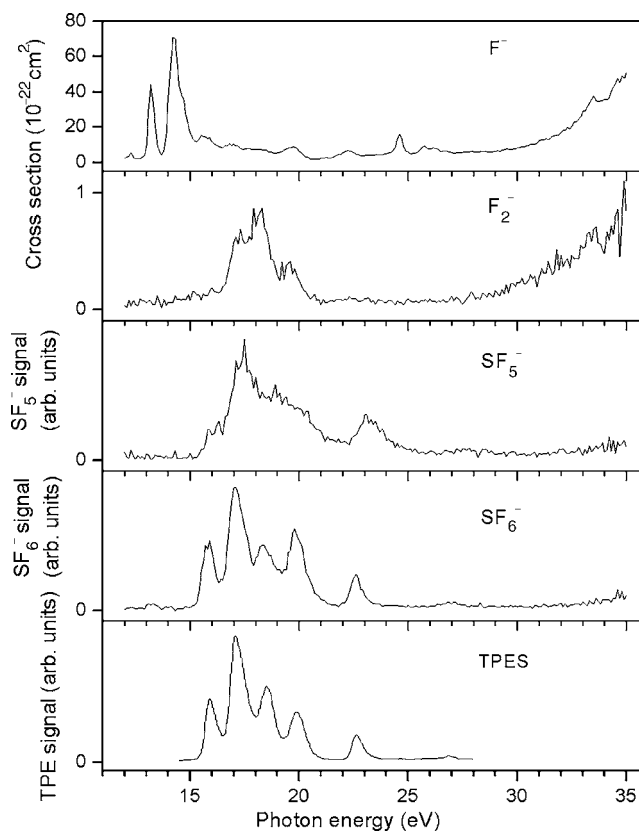


FIG. 1. Cross sections for anion production following photoexcitation of SF<sub>6</sub>. Note that the SF<sub>5</sub><sup>−</sup> and SF<sub>6</sub><sup>−</sup> spectra are not on an absolute scale. Ion yields were recorded as a function of photon energy between 12 and 35 eV with a step size of 0.1 eV and a wavelength resolution of 6 Å. These resolutions are equivalent to 0.07 eV at 12 eV and 0.6 eV at 35 eV. The ion yields are compared with the threshold photoelectron spectrum of SF<sub>6</sub> (Ref. 33).

## IV. RESULTS AND DISCUSSION

### A. SF<sub>6</sub>

The white light negative ion mass spectrum for SF<sub>6</sub> shows eight peaks corresponding to the anions F<sup>−</sup> (100%), F<sub>2</sub><sup>−</sup> (1%), SF<sup>−</sup> (<1%), SF<sub>2</sub><sup>−</sup> (<1%), SF<sub>3</sub><sup>−</sup> (<1%), SF<sub>4</sub><sup>−</sup> (<1%), SF<sub>5</sub><sup>−</sup> (2%), and SF<sub>6</sub><sup>−</sup> (67%). The relative signal strengths are shown in parentheses. All anion signals from SF<sub>6</sub> recorded as a function of photon energy are presented in Fig. 1, while Table I shows AE values of the anions, their cross sections, and quantum yields. For comparative purposes, Fig. 1 includes the threshold photoelectron spectrum (TPES) of SF<sub>6</sub>.<sup>33</sup> Poor signal strengths prevented ion yields for SF<sup>−</sup>, SF<sub>2</sub><sup>−</sup>, SF<sub>3</sub><sup>−</sup>, and SF<sub>4</sub><sup>−</sup> from being recorded. The F<sup>−</sup> and F<sub>2</sub><sup>−</sup> signals increase linearly with pressure, those of SF<sub>5</sub><sup>−</sup> and SF<sub>6</sub><sup>−</sup> nonlinearly with the rate of change increasing as pressure increases (Fig. 2).

Previous ion pair experiments have also observed SF<sub>5</sub><sup>−</sup> and SF<sub>6</sub><sup>−</sup> from SF<sub>6</sub>, their formation being attributed to electron attachment processes,<sup>24,26</sup>



TABLE I. Appearance energies, cross sections, and quantum yields for anions observed from photoexcitation of SF<sub>6</sub>, CF<sub>4</sub>, and SF<sub>5</sub>CF<sub>3</sub> in the range of 10–30 eV.

Molecule [AIE <sup>a</sup> (eV)]	Anion	AE <sup>b</sup> (eV)	Cross section maximum <sup>c</sup> (cm <sup>2</sup> )	Energy <sup>d</sup> (eV)	Quantum yield <sup>e</sup>
SF <sub>6</sub> [15.1]	F <sup>-</sup>	12.7	7.1 × 10 <sup>-21</sup>	14.2	2.4 × 10 <sup>-4</sup>
	F <sub>2</sub> <sup>-</sup>	16.3	8.7 × 10 <sup>-23</sup>	18.3	1.2 × 10 <sup>-6</sup>
	SF <sub>5</sub> <sup>-</sup>	15.1	— <sup>f</sup>	17.5	— <sup>g</sup>
	SF <sub>6</sub> <sup>-</sup>	15.1	— <sup>f</sup>	17.1	— <sup>g</sup>
CF <sub>4</sub> [15.4]	F <sup>-</sup>	13.0	1.4 × 10 <sup>-21</sup>	14.0	2.8 × 10 <sup>-5</sup>
	F <sub>2</sub> <sup>-</sup>	20.1	2.5 × 10 <sup>-23</sup>	21.6	3.5 × 10 <sup>-7</sup>
SF <sub>5</sub> CF <sub>3</sub> [12.9]	F <sup>-</sup>	11.05	3.4 × 10 <sup>-20</sup>	16.9	3.4 × 10 <sup>-4</sup>
	F <sub>2</sub> <sup>-</sup>	16.1	7.4 × 10 <sup>-22</sup>	17.9	7.1 × 10 <sup>-6</sup>
	SF <sup>-</sup>	24.0	1.4 × 10 <sup>-22</sup>	28.8	1.2 × 10 <sup>-6</sup>
	SF <sub>2</sub> <sup>-</sup>	20.2	1.4 × 10 <sup>-22</sup>	24.2	8.8 × 10 <sup>-7</sup>
	SF <sub>3</sub> <sup>-</sup>	15.4	2.9 × 10 <sup>-21</sup>	17.6	2.8 × 10 <sup>-5</sup>
	SF <sub>4</sub> <sup>-</sup>	13.0	2.9 × 10 <sup>-21</sup>	14.1	3.7 × 10 <sup>-5</sup>
	SF <sub>5</sub> <sup>-</sup>	13.0	— <sup>f</sup>	17.0	— <sup>g</sup>

<sup>a</sup>Adiabatic ionization energy. Values are taken from the observed onset of ionization for SF<sub>6</sub> (Ref. 34), CF<sub>4</sub> (Ref. 33), and SF<sub>5</sub>CF<sub>3</sub> (Ref. 13).

<sup>b</sup>Observed appearance energy (AE) from this work. We estimate the error to be ±0.2 eV, based on the resolution and step size used when recording ion yields.

<sup>c</sup>Cross section for anion production following photoexcitation of the parent molecule.

<sup>d</sup>Energy of strongest peak. It is at this energy, where appropriate, where cross section and quantum yield measurements are taken.

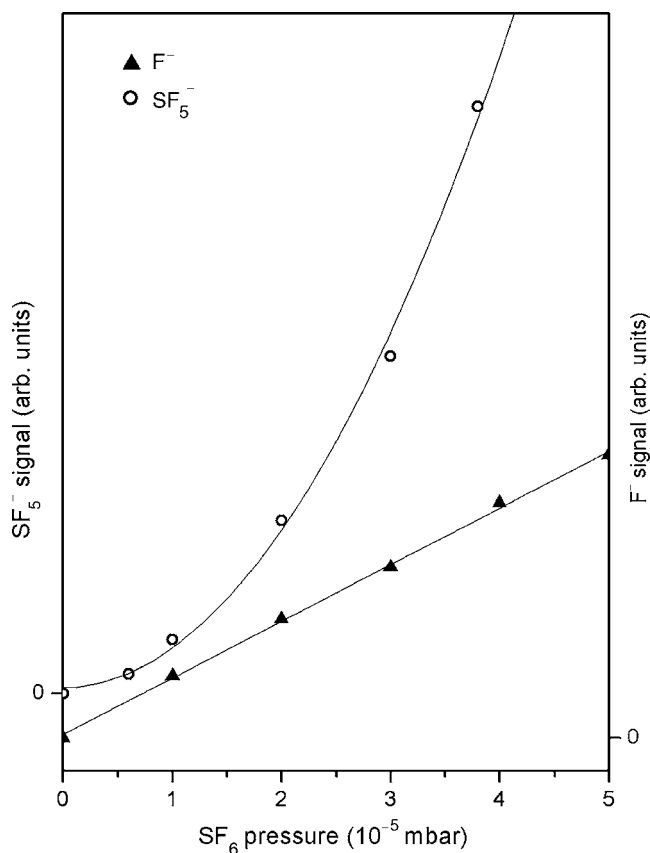
<sup>e</sup>Quantum yields for anion production, obtained by dividing cross sections for anions (column 4) by total photoabsorption cross sections. The latter values are given for SF<sub>6</sub>, CF<sub>4</sub>, and SF<sub>5</sub>CF<sub>3</sub> in Refs. 35, 2, and 20, respectively.

<sup>f</sup>Normalization of the signal strength to determine an effective cross section is not possible because of the nonlinear dependence of signal with pressure.

<sup>g</sup>Quantum yield cannot be determined because the cross section is not defined.

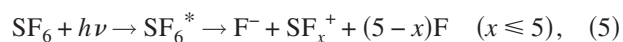


There can be little argument that reaction (3) must be responsible for the appearance of SF<sub>6</sub><sup>-</sup> and certainly SF<sub>6</sub> is a well-known electron scavenger, the rate coefficient at 300 K being  $(2.38 \pm 0.15) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$  (Ref. 11), which attaches zero-energy electrons with a very large cross section.<sup>36</sup> Furthermore, Fig. 1 highlights the striking similarities between the SF<sub>6</sub><sup>-</sup> spectrum and the SF<sub>6</sub> TPES. The only significant difference between the two is the peak at 19.9 eV, which appears stronger in the SF<sub>6</sub><sup>-</sup> spectrum. The same comparison has been discussed by Yenchu *et al.*<sup>34</sup> who compared their TPES of SF<sub>6</sub> with the ion yield of SF<sub>6</sub><sup>-</sup> produced from SF<sub>6</sub> reported by Mitsuke *et al.*;<sup>24</sup> the same discrepancy in relative signal strengths between the bands at 19.9 eV was observed. We note that the cross section for nondissociative electron attachment to SF<sub>6</sub> peaks at very low energy characteristic of *s*-wave capture,<sup>36</sup> but SF<sub>6</sub><sup>-</sup> anions observed from reaction (3) will arise from *all* electrons integrated under the  $\sigma$  versus electron energy distribution. By contrast, the TPES arises only from low-energy electrons detected within the bandpass of the threshold analyzer, approximately 4 meV.<sup>33</sup> In practice, the experimentally observed resolution will depend on a convolution of the electron energy distribution and the resolution of the photon source. In both experiments the monochromator resolution, approximately 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<sub>6</sub><sup>-</sup> spectra in Fig. 1 should be exactly the same, and this may

FIG. 2. Pressure dependence of F<sup>-</sup> and SF<sub>5</sub><sup>-</sup> anion signals from SF<sub>6</sub>.

explain the small differences that have been observed both by us and by Yench *et al.*<sup>34</sup> We also note that this difference may not be a particular property of SF<sub>6</sub> because a similar inconsistency in intensities in the threshold photoelectron and parent anion yields has been observed with another polyatomic molecule which attaches electrons very rapidly, cyclic-C<sub>5</sub>F<sub>8</sub>.<sup>37</sup> There are two observations from our work which provide evidence for SF<sub>5</sub><sup>-</sup> arising predominantly from reaction (4). First, the SF<sub>5</sub><sup>-</sup> signal increases nonlinearly when recorded as a function of pressure, consistent with the two-step mechanism represented by reactions (2) and (4); an anion signal arising from ion pair formation, SF<sub>6</sub> + *hν* → F<sup>+</sup> + SF<sub>5</sub><sup>-</sup>, would increase linearly with pressure. This is illustrated in Fig. 2 which clearly shows the contrast between the signal for the ion pair product, F<sup>-</sup>, and that for SF<sub>5</sub><sup>-</sup>. Second, the SF<sub>5</sub><sup>-</sup> ion yield shows many similarities to the TPES of SF<sub>6</sub>, whereas that of F<sup>-</sup> does not. However, these arguments do not exclude the possibility that a small amount of SF<sub>5</sub><sup>-</sup> is produced via the ion pair reaction above.

The F<sup>-</sup> and F<sub>2</sub><sup>-</sup> signals both increase linearly with pressure, and the following ion pair reactions are suggested as mechanisms for their formation,



Using enthalpies of formation at 298 K for F<sup>-</sup> of -249 kJ mol<sup>-1</sup> (Refs. 38 and 39), F<sub>2</sub><sup>-</sup> of -301 kJ mol<sup>-1</sup> (Ref. 40) and SF<sub>x</sub><sup>+</sup> given elsewhere,<sup>41</sup> the calculated enthalpies of reaction for Eq. (5) are 10.4, 15.0, 15.5, 19.6, and 23.7 eV for *x*=5-1, respectively. For reaction (6) they are 13.5, 13.8, 18.3, and 22.4 eV, for *x*=4-1, respectively. F<sup>-</sup> produced from reaction (5) has been observed before in the photon energy range of 11-31 eV and a detailed analysis performed.<sup>24</sup> Below 15.0 eV the associated cation can only be SF<sub>5</sub><sup>+</sup>, and the present work (Fig. 1) is in very good agreement with this earlier study. Scully *et al.* have observed the ion pair products F<sup>-</sup> and F<sub>2</sub><sup>-</sup> from SF<sub>6</sub> in the photon energy range of 20-205 eV.<sup>26</sup> Both fragment ions show broad bands centered at 35.5 eV. Although not photoexciting SF<sub>6</sub> above 35 eV, our study clearly shows the onsets for these features.

The F<sub>2</sub><sup>-</sup> spectrum in Fig. 1 shows features in the photon energy range of 16-21 eV which have not been observed before. Below 18.3 eV it is not possible to say whether the associated cation is SF<sub>4</sub><sup>+</sup> or SF<sub>3</sub><sup>+</sup>+F. The low F<sub>2</sub><sup>-</sup> cross section is reflected in its low signal strength, resulting in a poor signal-to-noise ratio. We identify three peaks centered 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.* found that the most prominent features in the F<sup>-</sup> ion yield at 13.2 and 14.3 eV were due to Rydberg transitions.<sup>24</sup> The peaks in the F<sub>2</sub><sup>-</sup> ion yield at 17.2, 18.2, and 19.7 eV approximately match with peaks in the TPES of SF<sub>6</sub> at 17.1, 18.5, and 19.9 eV, respectively. A similar observation is made in the F<sub>2</sub><sup>-</sup> ion yield from SF<sub>5</sub>CF<sub>3</sub> (Sec. IV C).

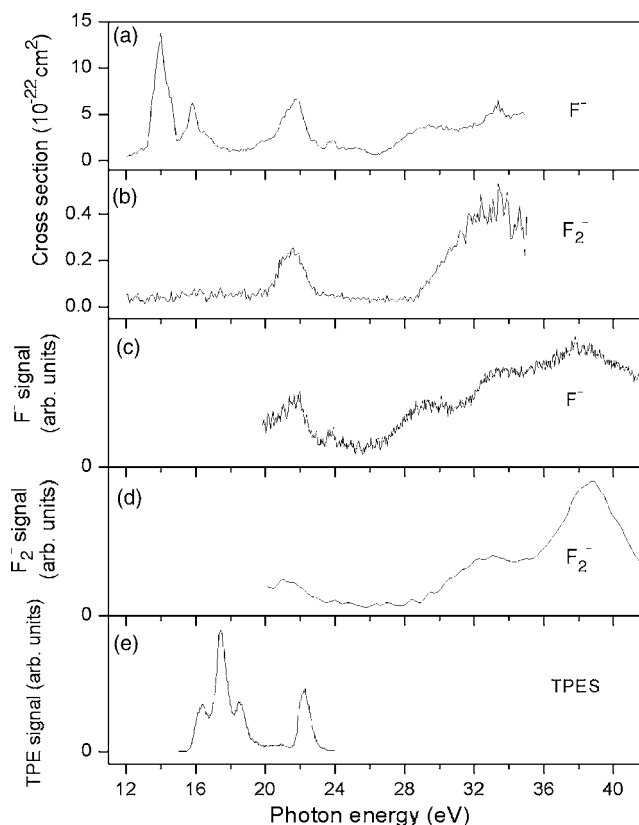
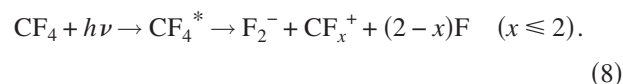


FIG. 3. Cross sections for anion production following photoexcitation of CF<sub>4</sub>. [(a) and (b)] F<sup>-</sup> and F<sub>2</sub><sup>-</sup> ion yields recorded as a function of photon energy between 12 and 35 eV with a step size of 0.1 eV and a wavelength resolution of 6 Å (this work). These resolutions are equivalent to 0.07 eV at 12 eV and 0.6 eV at 35 eV. The cross sections are on an absolute scale. [(c) and (d)] F<sup>-</sup> and F<sub>2</sub><sup>-</sup> ion yields from Scully (Ref. 31) recorded over a narrower energy range at higher resolutions of 0.5 and 2.0 Å, respectively. The cross sections are now on a relative scale. (e) Threshold photoelectron spectrum of CF<sub>4</sub> for comparison (Ref. 33).

## B. CF<sub>4</sub>

The white light negative ion mass spectrum for CF<sub>4</sub> shows three peaks corresponding to the anions F<sup>-</sup> (100%), CF<sup>-</sup> (1%), and F<sub>2</sub><sup>-</sup> (3%). The F<sup>-</sup> and F<sub>2</sub><sup>-</sup> signals were recorded as a function of photon energy and are shown in Figs. 3(a) and 3(b), along with the TPES of CF<sub>4</sub> [(Ref. 33), Fig. 3(e)] which is included for comparative purposes. The corresponding data are shown in Table I. The ion yield of CF<sup>-</sup> was not obtained due to the poor signal strength.

The F<sup>-</sup> and F<sub>2</sub><sup>-</sup> signals both increase linearly with pressure and the following ion pair reactions are suggested as mechanisms for their formation,



The calculated enthalpies of reaction of Eq. (7) are 11.3, 17.5, and 20.6 eV for *x*=3-1, respectively; for Eq. (8) they are 16.2 and 19.2 eV for *x*=2-1, respectively. The F<sup>-</sup> ion yield from reaction (7) recorded here is in good agreement with a previous study in the photon energy range of 12-31 eV reported by Mitsuke *et al.*<sup>25</sup> The F<sup>-</sup> and F<sub>2</sub><sup>-</sup> yields

are also in good agreement with those reported by Scully at higher resolution in the photon range of 20–35 eV [(Ref. 31), Figs. 3(c) and 3(d)], but absolute cross sections were not determined in this earlier work. It is immediately obvious from Fig. 3 that the  $F^-$  and  $F_2^-$  yields share a similar feature between 20 and 23 eV. Mitsuke *et al.* assigned this feature in the  $F^-$  yield to three Rydberg transitions ( $3t_2 \rightarrow npt_2$   $n=4, 5$ , and 6 at energies of 20.96, 21.16, and 21.45 eV, respectively) converging on the third excited valence state of  $CF_4^+$  ( $\tilde{C}^2T_2$ ).<sup>25</sup> The Rydberg states excited at these energies would 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.*<sup>42</sup> Autoionizing structure is observed from 20.3 to 21.6 eV, preceding the onset of the  $\tilde{C}^2T_2$  state of  $CF_4^+$ . This can be observed in the TPES (Fig. 3) as a slight rise above the baseline in the same energy range. We therefore propose 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 approximately 30 times larger than that for  $F_2^-$ . This may reflect the degree of coupling between states and/or the steric disadvantage on forming an extra bond to produce  $F_2^-$ .

The highest outer-valence electronic state of  $CF_4^+$  is the  $\tilde{D}^2A_1$  state at 25.1 eV, whereas the next discrete state in the photoelectron spectrum corresponding to ionization of the  $2t_2$  inner-valence electron is the  $\tilde{E}^2T_2$  state at 40.3 eV.<sup>33,43</sup> 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<sup>31</sup> which extends up to 110 eV. In particular, broad maxima in the  $F^-$  yield are observed at 29.4 and 33.5 eV [Fig. 3(c)] which cannot be assigned to a simple one-electron valence-Rydberg excitation. The most likely explanation of these features is the result of promotion of outer-valence  $4t_2$  and  $3t_2$  electrons into shape resonance states.  $\beta$ -parameter measurements from angle resolved photoelectron spectroscopy<sup>43</sup> suggest that shape resonances in  $CF_4$  do exist at energies of 10–15 eV above the IE of the outer-valence  $t_2$  orbitals, and the two broad peaks observed here in the  $F^-$  dissociation channel are approximately 12 eV above their respective ionization energies. Although the signal-to-noise ratio is inferior, there is some evidence for a shape resonance in the  $F_2^-$  yield at 33.5 eV, but there is clearly no such resonance at 29.4 eV [Fig. 3(d)]. If this is indeed true, the absence at 29.4 eV, in contrast to its presence at 33.5 eV, may result from the different character of the  $3t_2$  (C–F  $\sigma$  bonding) and  $4t_2$  (F  $2p\pi$  nonbonding) orbitals<sup>33</sup> or from different predissociation mechanisms. Shape resonances have also been observed in the  $F^-$  yield from  $SF_6$ .<sup>26</sup>

### C. $SF_5CF_3$

The white light negative ion mass spectrum for  $SF_5CF_3$  shows eight peaks corresponding to the anions  $F^-$  (100%),  $CF^-$  (1%),  $F_2^-$  (2%),  $SF^-$  (1%),  $SF_2^-$  (1%),  $SF_3^-$  (1%),  $SF_4^-$  (2%), and  $SF_5^-$  (14%). With the exception of  $SF_5^-$ , all of the anion signals increase linearly with pressure.  $SF_5^-$  formed

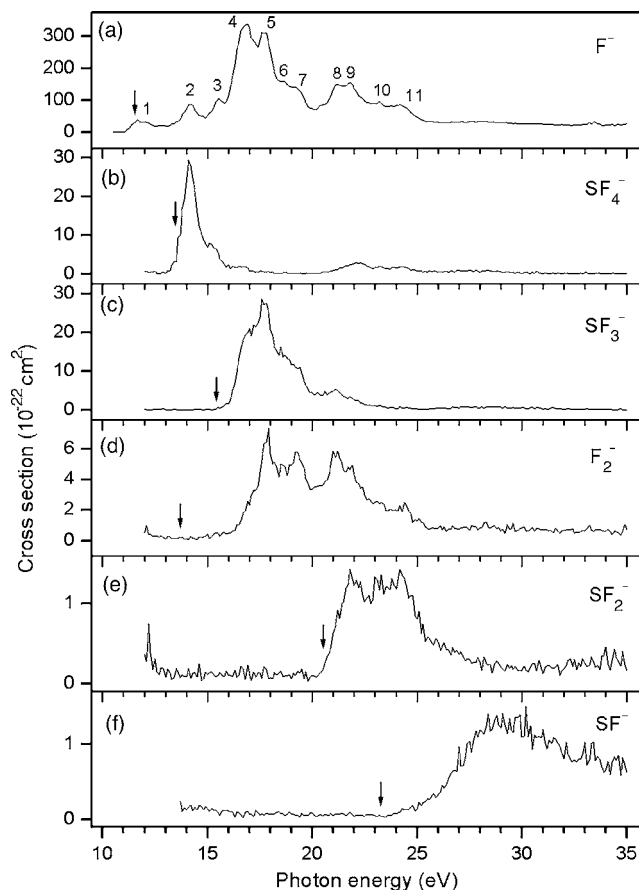
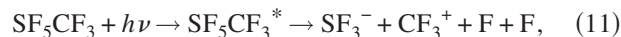
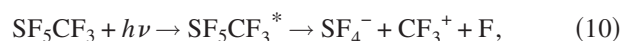
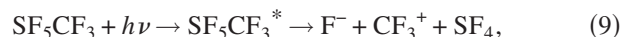


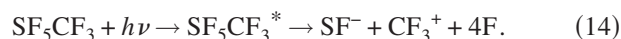
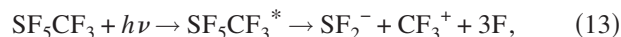
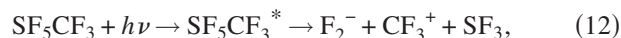
FIG. 4. Cross sections for anion production following photoexcitation of  $SF_5CF_3$ . Ion yields were recorded as a function of photon energy between 10.5 and 35.0 eV with a step size of 0.1 eV and a wavelength resolution of 6 Å. These resolutions are equivalent to 0.05 eV at 10.5 eV and 0.6 eV at 35 eV. Note that the  $F^-$  spectrum below 12 eV was recorded with the lower-energy grating, and the data spliced into the higher-energy spectrum. Solid arrows in the  $F^-$  through  $SF^-$  yields show energies of the thermochemical thresholds calculated for reactions (9)–(14), respectively.

following photoexcitation of  $SF_5CF_3$  shows similar pressure behavior to  $SF_5^-$  formation from  $SF_6$ , and is discussed in more detail in Sec. IV C 2.

### 1. Thermochemistry

Ion yields for the anions resulting from ion pair formation are presented in Fig. 4, the data in Table I. The quantum yields are all in the range of  $10^{-7}$ – $10^{-4}$ , consistent with those expected for a large polyatomic molecule.<sup>21,22</sup> All spectra were recorded with the higher-energy grating. The ion yield of  $F^-$  below 12 eV was also recorded with the lower-energy grating and LiF window to display the threshold region more clearly, and an  $AE_{298}$  value of  $11.05 \pm 0.05$  eV was determined. The following reactions are suggested as the main sources of formation of the anions:





In all cases the cation formed is CF<sub>3</sub><sup>+</sup>, the associated anion therefore resulting from the SF<sub>5</sub> part of SF<sub>5</sub>CF<sub>3</sub>. This is reflected in the results; five different anions containing sulfur are detected compared to one containing carbon, CF<sup>-</sup>, which was only just detected above the sensitivity limit of the apparatus. The S–C bond is most likely to be the weakest in the molecule, the 0 K dissociation energy measured as 3.86 ± 0.45 eV.<sup>16</sup> In addition, Xu *et al.* have calculated bond dissociation energies in SF<sub>5</sub>CF<sub>3</sub>, resulting in  $D_0(\text{SF}_5\text{CF}_2-\text{F}) > D_0(\text{F}-\text{SF}_4\text{CF}_3) > D_0(\text{SF}_5-\text{CF}_3)$ .<sup>44</sup> We cannot say conclusively that reactions (9)–(14) are responsible for all of the detected anion signals. Certainly, more channels become energetically accessible at higher energies. It is, however, interesting that the thermochemical thresholds for reactions (9)–(14) approximately reflect the observed AE values (Table I). The only apparent exception is reaction (12), F<sub>2</sub><sup>-</sup> production, where steric constraints on forming a new bond could be responsible. This trend can be visualized in Fig. 4 by vertical arrows representing the enthalpies of the calculated thermochemical thresholds, within the approximations outlined in Sec. III. These values for  $\Delta_f H^0_{298}$  are 11.6, 13.5, 15.4, 13.7, 20.6, and 23.2 eV for reactions (9)–(14), respectively. They were calculated using literature enthalpies of formation ( $\Delta_f H^0_{298}$  in kJ mol<sup>-1</sup>); SF<sub>5</sub>CF<sub>3</sub> = -1717 (Ref. 38), F = +79 (Ref. 38), F<sup>-</sup> = -249 (Refs. 38 and 39), F<sub>2</sub><sup>-</sup> = -301 (Ref. 40), CF<sub>3</sub><sup>+</sup> = +406 (Ref. 15), SF<sub>4</sub> = -763 (Ref. 38), SF<sub>4</sub><sup>-</sup> = -908 (Refs. 38 and 45), SF<sub>3</sub> = -503 (Ref. 38), SF<sub>3</sub><sup>-</sup> = -802 (Refs. 38 and 46), SF<sub>2</sub><sup>-</sup> = -384 (Refs. 38 and 45), and SF<sup>-</sup> = -207 (Refs. 38 and 47). No errors are given but there is significant uncertainty in some of these values, which probably explains why the calculated AE is sometimes greater than the experimental value (e.g., F<sup>-</sup> and SF<sub>4</sub><sup>-</sup> in Fig. 4). The formations of F<sup>-</sup> and F<sub>2</sub><sup>-</sup> over the complete energy range of 11–35 eV are unlikely to result exclusively from reactions (9) and (12), respectively, whereas the channels available to form the sulfur-containing anions are fewer. Indeed, the ion yields for F<sup>-</sup> and F<sub>2</sub><sup>-</sup> do show structure over a much wider energy range than those of SF<sub>x</sub><sup>-</sup> (x = 1–4).

## 2. Yield of SF<sub>5</sub><sup>-</sup>

The ion yields for F<sup>-</sup>, F<sub>2</sub><sup>-</sup>, and SF<sub>5</sub><sup>-</sup> are presented in Fig. 5 and compared to the TPES of SF<sub>5</sub>CF<sub>3</sub>.<sup>13</sup> SF<sub>5</sub><sup>-</sup> is the only anion detected which is *not* associated with ion pair formation. Three comparisons can be made between the behavior of SF<sub>5</sub><sup>-</sup> formed from SF<sub>5</sub>CF<sub>3</sub> and SF<sub>5</sub><sup>-</sup> formed from SF<sub>6</sub>. First, the SF<sub>5</sub><sup>-</sup> signal increases nonlinearly with pressure, with the rate of change of signal increasing as the pressure increases. Second, electron attachment to SF<sub>5</sub>CF<sub>3</sub> is dissociative forming SF<sub>5</sub><sup>-</sup> (and CF<sub>3</sub>) as the only significant channel.<sup>8–12</sup> Third, the ion yield of SF<sub>5</sub><sup>-</sup> shows many similarities to the TPES of SF<sub>5</sub>CF<sub>3</sub>. We therefore propose that the dominant mechanism for the production of SF<sub>5</sub><sup>-</sup> from

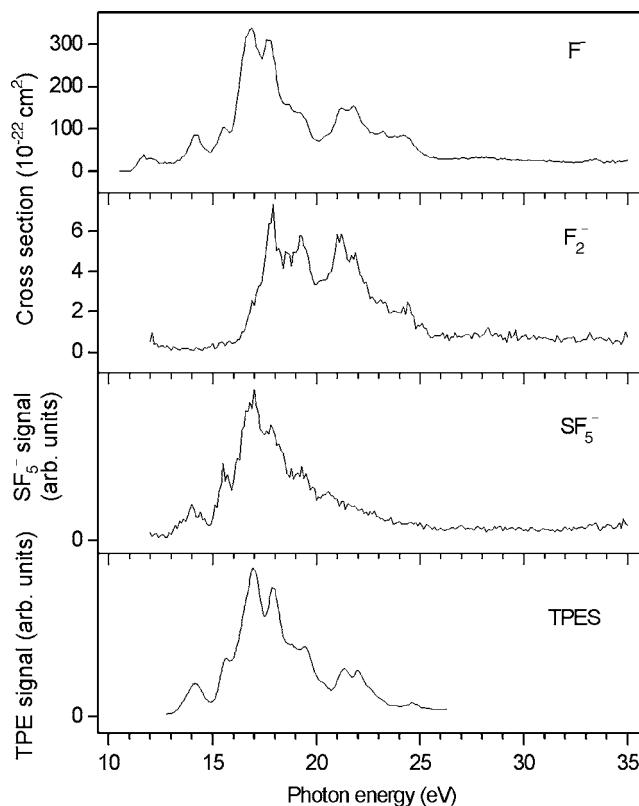
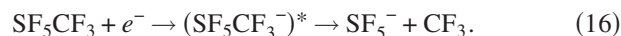
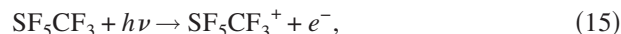


FIG. 5. Cross sections for anion production following photoexcitation of SF<sub>5</sub>CF<sub>3</sub>. Note that the SF<sub>5</sub><sup>-</sup> spectrum is not on an absolute scale. Ion yields were recorded as a function of photon energy between 10.5 and 35.0 eV with a step size of 0.1 eV and a wavelength resolution of 6 Å. These resolutions are equivalent to 0.05 eV at 10.5 eV and 0.6 eV at 35 eV. The ion yields are compared with the threshold photoelectron spectrum of SF<sub>5</sub>CF<sub>3</sub> (Ref. 13).

SF<sub>5</sub>CF<sub>3</sub> is dissociative electron attachment following photoionization as a source of low-energy electrons,



## 3. Discussion of the ion yields

As shown in Fig. 5, the F<sup>-</sup> and F<sub>2</sub><sup>-</sup> ion yields also show similarities to the TPES of SF<sub>5</sub>CF<sub>3</sub>. Due to its higher signal-to-noise ratio, it is in the F<sup>-</sup> spectrum where these similarities are most obvious. In the photon energy range of 13–23 eV the agreement between peak positions is good and the relative signal strengths show only small differences. The resemblance of the F<sup>-</sup> ion yield to the TPES could be explained by a process involving electron attachment being significant in F<sup>-</sup> formation. This has been the case in the discussion above, explaining the formation of SF<sub>5</sub><sup>-</sup> from both SF<sub>6</sub> and SF<sub>5</sub>CF<sub>3</sub>. However, the F<sup>-</sup> signal rises linearly with increasing gas pressure. This suggests strongly that a primary process, i.e., ion pair formation to F<sup>-</sup> + SF<sub>4</sub>CF<sub>3</sub><sup>+</sup> (or F<sup>-</sup> + CF<sub>3</sub><sup>+</sup> + SF<sub>4</sub>), is dominant.

For the purposes of this discussion the features in the F<sup>-</sup> ion yield are labeled in Fig. 4(a). The experimental AE(F<sup>-</sup>) is 11.05 eV, and this anion gives rise to peak 1 centered at 11.7 eV. This peak occurs below the onset of ionization for



TABLE II.  $F^-$  ion pair quantum yields ( $\Phi_{F^-}$ ) at energies below and above the onsets of ionization for  $SF_6$ ,  $CF_4$ , and  $SF_5CF_3$ . Cross sections from this work are normalized to photoabsorption cross sections for  $SF_6$  (Ref. 35),  $CF_4$  (Ref. 2), and  $SF_5CF_3$  (Ref. 20) to give values for  $\Phi_{F^-}$ .

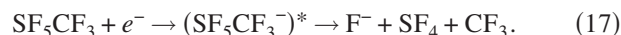
Molecule	$\Phi_{F^-}$ below onset of ionization	$\Phi_{F^-}$ above onset of ionization
$SF_6$	$2.4 \times 10^{-4}$ at 14.2 eV	$1.5 \times 10^{-5}$ at 24.6 eV
$CF_4$	$2.8 \times 10^{-5}$ at 14.0 eV	$9.3 \times 10^{-6}$ at 21.8 eV
$SF_5CF_3$	$1.5 \times 10^{-4}$ at 11.7 eV	$3.4 \times 10^{-4}$ at 16.9 eV

$SF_5CF_3$ , reported as 12.9 eV,<sup>13</sup> so the presence of photoelectrons from reaction (15) is not relevant. The energy of peak 1 is close to peaks observed in the  $SF_5CF_3$  photoabsorption<sup>20</sup> and total fluorescence yield<sup>48</sup> spectra at 11.4 eV. These two studies give different assignments to this transition. Holland *et al.*<sup>20</sup> assigned it to a blend of several valence-valence transitions, while Ruiz *et al.*<sup>48</sup> assigned it to a valence-Rydberg transition from the  $29a'$  highest-occupied molecular orbital of  $SF_5CF_3$  to a  $4s$  Rydberg orbital. The contribution of fluorescence at this energy was reported to originate from the  $CF_3$  fragment, following dissociation of  $SF_5CF_3^*$  and production of an excited electronic state of the  $CF_3$  radical. In addition, this was the most intense band observed within the photon energy range studied of 10–28 eV.<sup>48</sup> It must represent a transition to the same intermediate state which predissociates into states yielding both  $CF_3^*$  and  $F^-$  anions. We determine the ion pair quantum yield at the maximum of the peak in the  $F^-$  ion yield at 11.7 eV to be  $\Phi = 1.5 \times 10^{-4}$ . This small value, coupled with the fact that fluorescence from  $SF_5CF_3^*$  is unlikely to have a large quantum yield, suggests strongly that predissociation into neutral fragments is the favored process at this energy. A similar conclusion was reached by Shaw *et al.* in a comparable study of the dissociation dynamics of Rydberg states of some substituted methane molecules.<sup>23</sup> The agreement of peak positions in  $SF_5CF_3$  between the photoabsorption spectrum,<sup>20</sup> the total fluorescence yield<sup>48</sup> and the  $F^-$  ion yield extends up to 17 eV, but above this energy similarities between the spectra are less clear.

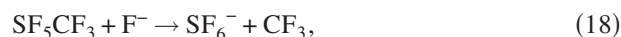
It is interesting that the  $F^-$  ion pair quantum yield does not decrease above the onset of ionization of  $SF_5CF_3$ , 12.9 eV. Features 1 and 4 at 11.7 and 16.9 eV, for example, have  $\Phi = 1.5 \times 10^{-4}$  and  $3.4 \times 10^{-4}$ , respectively (Table II). As a result of significant photoabsorption leading to ionization, one might expect the ion pair quantum yield to decrease, as observed for both  $SF_6$  and  $CF_4$  (Table II). However, above the IE of  $SF_5CF_3$  the  $F^-$  ion yield increases, approximately matching the shape of the TPES. In fact, features 2–11 of Fig. 4(a) occur at, or just below, vertical ionization energies in the TPES of  $SF_5CF_3$ .<sup>20</sup> Only feature 1 does not follow this trend. It seems unlikely that valence states of  $SF_5CF_3$  which predissociate into ion pairs coincidentally lie very close to the ionization thresholds, certainly across this large energy range. It is much more likely that Rydberg states play an important role. Certainly the  $F^-$  ion yield would be explained if coupling to ion pair states was more significant from Rydberg states close to the ionization 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 ionization energy,<sup>21</sup> so by definition it is the low- $n$  states which have been the most widely studied. The difficulties in assigning peaks in the total fluorescence yield spectrum of  $SF_5CF_3$  have already been noted by Ruiz *et al.*,<sup>48</sup> and at our modest resolution there are several valence-Rydberg transitions which could be assigned to peaks 2–11 in Fig. 4(a). We simply comment that a much higher-resolution spectrum would be needed for such a large molecule in order to give definitive assignments.

An alternative mechanism than reaction (9) for production of  $F^-$  might be via dissociative electron attachment to  $SF_5CF_3$ , e.g.,



We reject this because it is well known that the only product of low-energy electron attachment to  $SF_5CF_3$  is  $SF_5^-$  [reaction (16)],<sup>8–12</sup> and we note the huge signal of the  $F^-$  ion yield to the relatively weak signal of  $SF_5^-$  (Fig. 5). Furthermore, the only way that the  $F^-$  signal could show a linear dependence with pressure of  $SF_5CF_3$  in these circumstances if, in addition, there was another reaction removing  $F^-$ , e.g.,



and the relative rate coefficient for reactions (16)–(18) were “correct.” We regard this as speculative and highly unlikely.

This analysis also extends to the ion yields for  $SF_4^-$ ,  $SF_3^-$ ,  $F_2^-$ ,  $SF_2^-$ , and  $SF^-$ . The peak positions and the extent of structure observed for these anions can be explained in the same way as the  $F^-$  ion yield. The thermochemical considerations outlined in Sec. IV C 1 are also relevant. The  $SF_4^-$ ,  $SF_3^-$ , and  $SF_2^-$  ion 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 ionization energies. We suggest the number of available ion pair states reflects the structure seen in the ion yields.  $SF_4^-$ , for example, is likely to arise from reaction (10) only. It is certainly the most sterically viable channel. Coupling of high-lying Rydberg states to this ion-pair state will give rise to the peaks at 14 and 15 eV [Fig. 4(b)]. Lack of structure above 16 eV represents the point where this ion pair state no longer couples significantly to Rydberg states.  $SF_3^-$  and  $SF_2^-$  also arise through coupling of high-lying Rydberg states to an appropriate ion pair state and only over a limited energy range above the onset. In contrast, many more dissociation channels will be available to yield the anions  $F^-$  and  $F_2^-$ . As a result, structure in both ion yields extends extensively from onset up to 25 eV. Finally, it is noted that shape resonances have been observed in the yields of many anions in both  $SF_6$  and  $CF_4$  above 25 eV.<sup>26,31</sup> There

is no obvious evidence for such peaks in our ion yields from SF<sub>5</sub>CF<sub>3</sub>, but it would be surprising if they were not present.

## V. CONCLUSIONS

The peaks in the F<sup>-</sup> yields from both SF<sub>6</sub> and CF<sub>4</sub> have been assigned to Rydberg transitions,<sup>24,25</sup> and the assignments are not repeated here. However, there is some disagreement whether the transitions observed in the VUV absorption spectrum of SF<sub>5</sub>CF<sub>3</sub>,<sup>6,20</sup> and indeed the CF<sub>3</sub><sup>\*</sup> fluorescence excitation spectrum,<sup>48</sup> is due to intravalence or Rydberg transitions. Peaks in the absorption and electron energy loss spectra of SF<sub>5</sub>CF<sub>3</sub> were assigned by Limao-Vieira *et al.*<sup>6</sup> to valence-Rydberg transitions, and quantum defects determined. Ruiz *et al.*<sup>48</sup> also assigned peaks in the absorption spectrum that led to CF<sub>3</sub> fluorescence to valence-Rydberg transitions. Holland *et al.*,<sup>20</sup> however, assigned the main peaks in the absorption spectrum to valence-valence transitions. Our spectra observe a different exit channel, i.e., photodissociation of excited states of SF<sub>5</sub>CF<sub>3</sub> to production of anions. However, the primary excitation process in all these experiments is the same, and we favor their assignment to Rydberg transitions, 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.<sup>21,22</sup> Second, apart from the low-energy peak in the F<sup>-</sup> yield at 11.7 eV below the IE of SF<sub>5</sub>CF<sub>3</sub>, all the F<sup>-</sup> 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 SF<sub>5</sub>CF<sub>3</sub><sup>+</sup>, it seems very likely that these F<sup>-</sup> peaks correspond to photoexcitation of Rydberg states.

A summary of the numerical information obtained from the ion yields from SF<sub>6</sub>, CF<sub>4</sub>, and SF<sub>5</sub>CF<sub>3</sub> is given in Table I, listing AEs of anions, cross sections, and quantum yields. The anions observed from SF<sub>5</sub>CF<sub>3</sub> were all seen in either the SF<sub>6</sub> or CF<sub>4</sub> study. The signal strengths from the SF<sub>x</sub><sup>-</sup> anions, however, were marginally stronger from SF<sub>5</sub>CF<sub>3</sub> than from SF<sub>6</sub>, allowing their ion yields to be recorded. Unsurprisingly, F<sup>-</sup> and F<sub>2</sub><sup>-</sup> were observed from all three molecules. The most prominent features in the F<sup>-</sup> ion yields from SF<sub>6</sub> and CF<sub>4</sub> occur below the onset of ionization. This is not the case for F<sup>-</sup> from SF<sub>5</sub>CF<sub>3</sub>. This observation is clearly demonstrated in Table II when comparing the ion pair quantum yields of F<sup>-</sup> above and below the onset of ionization for these three molecules.

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