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DOI:

[10.1016/S0009-2614\(02\)01763-3](https://doi.org/10.1016/S0009-2614(02)01763-3)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Chim, RYL, Kennedy, R & Tuckett, R 2003, 'The vacuum-UV absorption spectrum of SF₅CF₃; implications for its lifetime in the earth's atmosphere', *Chemical Physics Letters*, vol. 367, no. 5-6, pp. 697-703.
[https://doi.org/10.1016/S0009-2614\(02\)01763-3](https://doi.org/10.1016/S0009-2614(02)01763-3)

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Absorption spectrum of SF₅CF₃ in the range 8-20 eV ; implications for its atmospheric lifetime

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Chem. Phys. Letts., (2003) **367**, 697-703.

DOI: 10.1016/S0009-2614(02)01763-3

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Professor Richard Tuckett (University of Birmingham) / July 2011

The vacuum-UV absorption spectrum of SF₅CF₃ ; implications for its lifetime in the earth's atmosphere

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Number of pages : 9 (including references and figure captions)
Number of figures : 2
Number of tables : 2

Running title : VUV absorption spectrum of SF₅CF₃

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Abstract : Using vacuum-UV radiation from a synchrotron source, the absorption spectrum of SF₅CF₃ has been measured in the range 50-150 nm at a resolution of 0.12 nm. The cross section at the Lyman- α wavelength of 121.6 nm is $1.5 \pm 0.3 \times 10^{-17}$ cm² molecule⁻¹. The loss of SF₅CF₃ on a molecular basis from the earth's atmosphere is dominated, not by photon-induced dissociation, but by electron attachment in the mesosphere above 60 km, yielding SF₅⁻. The lifetime of SF₅CF₃ in the earth's atmosphere, however, is determined primarily by the meteorological conditions that transport it from the earth's surface to the mesosphere, and not by processes that occur in that region. By comparison with data for SF₆, a lifetime of *ca.* 1000 years for SF₅CF₃ is estimated.

1. Introduction

Two years ago, a compound previously undetected in the earth's atmosphere, trifluoromethyl sulfur pentafluoride (SF_5CF_3), was reported by Sturges *et al.* [1]. Its origin is believed to be anthropogenic. The most likely source is the reaction of the $\text{SF}_5\cdot$ radical, a breakdown product of the dielectric SF_6 in high voltage equipment, with $\text{CF}_3\cdot$ radicals on the surface of fluoropolymers. Measurements made in Antarctica of air samples pumped out of deep consolidated snow (firn) at various depths from the surface were compared with the depth profiles to be expected based on certain atmospheric scenarios. These data suggest that the concentration of SF_5CF_3 in the earth's atmosphere is still very small, *ca.* 0.12 parts per trillion, but growing at approximately 6% per annum, the same growth rate as SF_6 . Stratospheric profiles, determined from air collected by balloons launched from the northern hemisphere, suggest that the lifetime of this species in the atmosphere is very long, between several hundred and a few thousand years. Laboratory infra-red absorption measurements [1] have shown that SF_5CF_3 has the highest radiative forcing per molecule of any pollutant released into the atmosphere to date ($0.57 \text{ W m}^{-1} \text{ ppb}^{-1}$). The global warming potential (GWP) is estimated to be 18000, with only SF_6 having a higher value.

The processes that remove a pollutant from the earth's atmosphere include reaction with the $\text{OH}\cdot$ radical in the troposphere ; UV photolysis (200-300 nm) and reactions with $\text{O} (^1\text{D})$ in the stratosphere ; and reactions with small cations, free electrons and vacuum-UV (VUV) photons (especially at the Lyman- α wavelength of 121.6 nm) in the upper stratosphere and mesosphere. Although not yet measured, we believe that the reactions of both $\text{OH}\cdot$ and $\text{O} (^1\text{D})$ with SF_5CF_3 , like those with CF_4 and SF_6 [2], will be very slow ($< 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). UV photolysis in the lower stratosphere seems very unlikely because the S-C bond strength has been measured indirectly by photoelectron – photoion coincidence spectroscopy to be as high as $4.06 \pm 0.45 \text{ eV}$ [3], similar to that of the S-F bond in SF_6 [4]. Short wavelength light ($\lambda = 200\text{-}300 \text{ nm}$) which reaches the stratosphere has enough energy to photodissociate SF_5CF_3 . The cross section at these wavelengths close to threshold, however, is expected to be very small, as the electronic transition is from a bound to a repulsive state. Indeed, no absorption has been observed for $\lambda > 190 \text{ nm}$, and electron energy loss spectroscopy (EELS) has shown that, for vertical excitation, the lowest-lying excited electronic state of SF_5CF_3 lies more than 8 eV ($\lambda < 155 \text{ nm}$) above the ground state [5].

Interest has therefore centred on the reactions that could remove SF_5CF_3 in the upper stratosphere and mesosphere above *ca.* 60 km. The total rate of removal of SF_5CF_3 , in units of molecules per unit volume per unit time, by its reactions with cations, electrons and Lyman- α (121.6 nm) photons is given by :

$$\text{Rate} = [\text{SF}_5\text{CF}_3] \cdot \left(\sum_{\text{ions}} k_{\text{ion}}[\text{ion}] + k_e[e^-] + \sigma_{121.6} J_{121.6} \right) \quad (1)$$

where k_{ion} and k_e are the bimolecular rate constants for reactions of a cation or electron with SF_5CF_3 , $\sigma_{121.6}$ and $J_{121.6}$ are the absorption cross-section of SF_5CF_3 and the mesospheric solar flux at 121.6 nm, and the square brackets signify the concentration of a species. The value of $J_{121.6}$ is well established [6]. We note that equation (1) assumes that an ion-molecule reaction, electron attachment and VUV absorption leads to the removal of every SF_5CF_3 molecule by the formation of dissociation products. This assumption is true for ion-molecule reactions, but is not necessarily so for the other two processes.

The rate constants for reactions of SF_5CF_3 with a large number of small cations have been measured in a selected ion flow tube apparatus at 298 K [7,8]. Most reactions proceed with rate constants close to the capture limit. However, those of the most abundant ions in the mesosphere (O_2^+ and NO^+ [9]) have rate constants which are very much slower, due to the low recombination energies of these ions. Thus, ion-molecule reactions are unlikely to contribute significantly to the total removal rate of SF_5CF_3 from the atmosphere. Electron attachment experiments have been performed in *ca.* 1 bar of N_2 and Ar buffer gases at 298 K under non-thermal swarm conditions [10]. The rate constant was measured as a function of mean electron energy in the range 0.04 – 1.90 eV, with k_e increasing as the mean electron energy decreases. The electron attachment rate constant with thermal electrons at 298 K, $\bar{\varepsilon} = 0.038$ eV, was estimated to be $7.7 \pm 0.6 \times 10^{-8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and significantly the only observed product was SF_5^- from dissociative attachment. These results have been confirmed by others [11,12]. This process therefore does remove SF_5CF_3 from the earth's atmosphere, and Kennedy and Mayhew, like others before for both SF_5CF_3 and SF_6 [2,11-13], assumed that it was dominant. In this Letter we report the first observation of the absorption cross section of SF_5CF_3 in the VUV, and especially at the Lyman- α wavelength of 121.6 nm where the solar mesospheric flux is the greatest. As mentioned earlier, a pseudo-absorption spectrum has been measured by EELS at a resolution of *ca.* 0.5 eV [5]. The data could not be put on to an absolute scale of photon absorption cross section as a function of energy. It was noted, however, that SF_5CF_3 , certainly unlike CF_4 [2], did absorb significantly at 121.6 nm. The third term of the right hand side of eq.(1) may therefore contribute significantly to the total removal rate of SF_5CF_3 from the earth's mesosphere, leading to a decrease in the lifetime of SF_5CF_3 in the atmosphere.

2. Experimental

The VUV absorption apparatus has been described elsewhere [14]. Radiation from a synchrotron passes through the exit slit of a VUV monochromator, through a 2-stage differential pumping section, and through a 1 mm thick stainless steel microchannel plate into an absorption cell of length, L , 300 mm. A

pressure differential of 1000:1 across the microchannel plate is possible. The gas pressure in the absorption cell, in the range 5-60 μbar , is measured by a Balzers capacitance manometer, and is maintained constant *via* a slow controlled flow of gas. The VUV radiation at the end of the cell is detected through a sodium-salicylate-coated window and a visible photomultiplier tube operating in the photon counting mode. Since the pressure of gas and optical path length are known, measurement of the ratio of transmitted intensity observed for background (no gas) and sample spectra (with gas) can yield, *via* the Beer Lambert law, absolute absorption cross sections. In the calculation of I_o/I at every value of the VUV energy, allowance is made for the natural decay of the VUV flux over the time of an experiment. No allowance is made for the small pressure gradient within the absorption cell due to gas leakage through the microchannel plate, and the small effects of second-order radiation from the VUV monochromator are ignored. We estimate that cross sections are accurate to *ca.* 15-20 %.

Preliminary experiments were performed at the Bessy I source in Berlin using the 1.5 m NIM-2 beamline with a laminar 1200 l/mm gold-coated Zeiss grating. Using 100 μm entrance and exit slits giving a photon resolution of *ca.* 0.08 nm, the absorption spectrum of CF_4 in the range 10-40 eV is shown in Figure 1. The cross-section at 10.2 eV, Lyman- α radiation, is too small to measure accurately, but has been measured by Ravishankara *et al.* [2] to be less than $8 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$. Our spectrum is in good agreement with that recorded by Lee *et al.* [15] at an inferior resolution of 0.2 nm. In particular, the $(1t_1)^{-1}3p$, $(4t_2)^{-1}3s$ and $(1e)^{-1}3p/(4t_2)^{-1}3d$ Rydberg states at 13.6, 13.9 and 15.9 eV are clearly observed [16]. The cross sections at the maxima of the well-resolved first and third peaks are 5.5×10^{-17} and $5.8 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, in excellent agreement with the values obtained by Lee *et al.* [15]. The absorption spectrum of SF_5CF_3 was obtained using beamline SA63 of the Super-Aco synchrotron source in Paris, with a 1 m normal incidence monochromator equipped with a 1200 l/mm grating. Using a photon resolution of 0.12 nm, the absorption spectrum in the range 6-26 eV is shown in Figure 2. The widths of the peaks are determined by molecular properties and not by the resolution of the incident VUV beam, since the spectrum is invariant to the slitwidth of the monochromator. The spectrum up to 12.4 eV (100 nm) is in good agreement with that obtained by EELS, which approximates to absorption spectroscopy for high incident electron energies, although absolute values of σ were not determined [5]. We determine that the cross section of SF_5CF_3 at 10.2 eV, Lyman- α radiation, is $1.5 \pm 0.3 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1}$, where the Beer-Lambert law is expressed as $\ln(I_o/I) = \sigma L[\text{SF}_5\text{CF}_3]$. No attempt has been made to assign the peaks in the spectrum, although peaks below 14.1 eV, the vertical ionisation energy to the ground state of SF_5CF_3^+ [3], must correspond to Rydberg states of SF_5CF_3 converging on either the ground or excited states of SF_5CF_3^+ .

3. The lifetime of SF_5CF_3 in the earth's atmosphere

The values for the electron attachment rate constant, the absorption cross-section at 121.6 nm, and atmospheric lifetimes of CF₄, SF₆ and SF₅CF₃ are given in Table 1. The almost infinite value for the lifetime of CF₄, greater than 50000 years [2,18], arises because this molecule shows no absorption at 121.6 nm, attaches electrons at a negligibly slow rate, and does not react with O₂⁺ or NO⁺. By comparison, SF₆ and SF₅CF₃ both attach electrons at a fast rate (greater than 10⁻⁸ cm³ molecule⁻¹ s⁻¹) and show significant absorption with Lyman- α radiation. Furthermore, the height profiles of SF₆ and SF₅CF₃ are similar in the atmosphere [1]. It is therefore sensible to make quantitative comparisons between these two molecules. We note that k_e for SF₅CF₃ at 298 K is three times smaller than for SF₆, whereas the absorption cross-section is 8.5 times larger. Therefore, the pseudo-first-order rate constant for removal of SF₅CF₃ by electrons divided by that due to photons at the same altitude of the mesosphere, $k_e[e^-] / \sigma_{121.6}J_{121.6}$, is 25.5 times smaller than this ratio for SF₆. (This assumes that electron attachment leads to total destruction of SF₆, to SF₅⁻.) Assuming an incorrect value for k_e of 1 x 10⁻⁹ cm³ molecule⁻¹ s⁻¹, Ravishankara *et al.* [2] determined that this ratio of pseudo-first-order rate constants for SF₆ was 3.2, and obtained an atmospheric lifetime of 3200 years. Using the much larger and correct value for k_e (SF₆) of 2.3 x 10⁻⁷ cm³ molecule⁻¹ s⁻¹, Morris *et al.* [13] showed that this ratio of pseudo-first-order rate constants was 1998, and determined a lower limit to the atmospheric lifetime of 800 years. The lower limit arises because they assumed that every electron attachment event led to the permanent removal of SF₆ from the atmosphere. Reddmann *et al.* [20] considered a number of scenarios for the destruction of SF₆⁻. They found that if less than 100 % was destroyed, the lifetime was increased ; they calculated values spanning 400 to 10000 years, depending on the loss mechanism and the value for the electron density in the upper stratosphere / mesosphere.

Assuming that the analysis of Morris *et al.* [13] for SF₆ is correct, then the predominant removal process for SF₅CF₃ remains electron attachment and not VUV photolysis, since the ratio of the pseudo-first-order rate constants for SF₅CF₃ is 1998 / 25.5 or 78.3, *i.e.* still much greater than unity. It is more difficult, however, to convert these first-order rate constants into an atmospheric lifetime for SF₅CF₃. The chemical lifetime, τ_{chemical} , can be written as $1 / (k_e[e^-] + \sigma_{121.6}J_{121.6})$, but the value obtained is a function of position, particularly altitude, in the atmosphere. In the troposphere, τ_{chemical} will be infinite because both the concentration of electrons and $J_{121.6}$ are effectively zero at low altitude, but in the mesosphere it will be much less. Put another way, multiplication of k_e for either SF₆ or SF₅CF₃ by a typical electron density in the mesosphere, 10¹–10³ cm⁻³ [9], yields a chemical lifetime for either species which is much shorter than the average atmospheric lifetime, simply because most of the SF₆ or SF₅CF₃ does not reside in the mesosphere.

Global atmospheric lifetimes, such as those reported for SF₆ [2,13], are obtained from globally-averaged loss frequencies. In forming the average, the pseudo-first-order destruction rate constant for each region of the atmosphere is weighted according to the number of molecules of compound in that region,

$$\langle k \rangle_{global} = \frac{\sum_i k_i V_i n_i}{\sum_i V_i n_i} \quad (2)$$

where i is a region, k_i is a pseudo-first-order rate constant for region i , V_i is the volume of region i , and n_i is the number density of the compound under study in region i . The averaging process thus needs input from a 2-D or 3-D model of the atmosphere in order to supply the values of n_i . Differences in the kinetic model (k_i) and the atmospheric distributions (n_i) from different climate / transport models account for the variety of atmospheric lifetimes that have been reported [2,13,20]. For molecules such as SF₆ which are only destroyed in the mesosphere above 60 km, the importance of both these factors has been explored by Hall and Waugh [21]. Their results show that because the fraction of the total number of SF₆ molecules in the mesosphere is very small, the global atmospheric lifetime is very much longer than the mesospheric, chemical lifetime. Thus, they quote that if the mesospheric loss frequency is $9 \times 10^{-8} \text{ s}^{-1}$, corresponding to a local lifetime of 129 days, then the global lifetime ranges between 1424 and 1975 years, according to which climate / transport model is used.

SF₆ attaches electrons with a temperature-independent rate constant close to the theoretical limit for s-wave capture of $ca. 2 \times 10^{-7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [19]. Morris *et al.* [13] assume complete destruction of the transient SF₆⁻ anion and determine a lower limit to the atmospheric lifetime of 800 years. They conclude that the inclusion of electron attachment reactions can never reduce the lifetime of any long-lived greenhouse molecule, such as SF₅CF₃, below this limit of 800 years. Very recently, Miller *et al.* [12] have measured the electron attachment rate constant to SF₅CF₃ as a function of temperature in the range 296-563 K. Their value at room temperature is in excellent agreement with the estimate of Kennedy and Mayhew [10], they determine that k_e decreases very slightly with decreasing T, and deduce an activation barrier of 2.4 kJ mol⁻¹. By extrapolating their data to 250 K, an average temperature in the mesosphere, they estimate that k_e (SF₅CF₃) at this temperature is 4 times smaller than that of SF₆, but approximately 4 times larger than that of c-C₄F₈. Since the lower-limit lifetime of the former is 800 years and that of the latter 1400 years [13], Miller *et al.* [12] deduce that the lifetime of SF₅CF₃ is probably of the order of 1000 years.

To improve the kinetic part of the atmospheric destruction model for SF₅CF₃ from which the lifetime is obtained, knowledge is needed of the fate of transient SF₅CF₃⁻ anions formed by the attachment of

thermal-energy electrons, and of excited SF_5CF_3^* produced by photoexcitation at 121.6 nm. Some destruction pathways are listed in Table 2. The feasibility of these pathways can be assessed by combining literature 0 K thermochemical data for CF_3 , CF_3^+ , CF_3^- , SF_5 , SF_5^+ and SF_5^- with the 0 K enthalpy of formation of SF_5CF_3 . The values adopted for CF_3 , CF_3^+ , CF_3^- , SF_5 , SF_5^+ and SF_5^- are given in brackets in Column 1 of Table 2, in units of kJ mol^{-1} . There are two recent theoretical values for $\Delta_f H^0$ (SF_5CF_3), $-1621 \text{ kJ mol}^{-1}$ (G2 [22]) and $-1623 \text{ kJ mol}^{-1}$ (MP2 [12]). The JANAF tables quote $\Delta_f H^0$ (SF_5CF_3) = $-1700 \pm 63 \text{ kJ mol}^{-1}$ [23]. A recent determination of the dissociative ionisation energy of SF_5CF_3 (*i.e.* $\Delta_f H^0$ for the reaction $\text{SF}_5\text{CF}_3 \rightarrow \text{CF}_3^+ + \text{SF}_5 + e^-$) yielded $\Delta_f H^0$ (SF_5CF_3) = $-1770 \pm 47 \text{ kJ mol}^{-1}$ [3]. Using the G2 value for $\Delta_f H^0$ (SF_5CF_3) from Ball [22] (Scheme A in Table 2), dissociative attachment of a zero-energy electron to SF_5CF_3 to form $\text{SF}_5^- + \text{CF}_3$ is energetically feasible, but the products cannot be $\text{CF}_3^- + \text{SF}_5$. This is consistent with the results of the electron attachment experiments performed in N_2 and Ar buffer gases [10], where the only observed product ion was SF_5^- . With Lyman- α photoexcitation (10.2 eV), the limit $\text{SF}_5 + \text{CF}_3$ is easily accessible. It is also possible to reach the ion-pair limit $\text{CF}_3^+ + \text{SF}_5^-$, but not $\text{SF}_5^+ + \text{CF}_3^-$. Using the more negative experimental value for $\Delta_f H^0$ (SF_5CF_3) from Chim *et al.* [3] (Scheme B in Table 2), the same conclusions hold except electron attachment to form $\text{SF}_5^- + \text{CF}_3$ becomes marginally endothermic by 25 kJ mol^{-1} . The main conclusion from the data of Table 2 is that energetically-accessible exit channels in which the S–C bond is broken exist for both zero-energy electron attachment to SF_5CF_3 and Lyman- α photoexcitation of SF_5CF_3 . Both processes, therefore, are likely to destroy SF_5CF_3 with unit efficiency.

4. Conclusions

We have measured the vacuum-UV absorption cross-section of SF_5CF_3 in the range 50-150 nm. The cross-section at 121.6 nm is $1.5 \pm 0.3 \times 10^{-17} \text{ cm}^2$. By comparison with data for SF_6 , we deduce that electron attachment in the mesosphere is the dominant removal process of SF_5CF_3 from the earth's atmosphere, with VUV photodissociation only contributing *ca.* 1 % to the pseudo-first-order rate constant. The atmospheric lifetime, however, is determined primarily by the rate of transport of SF_5CF_3 from the earth's surface to the mesosphere. We agree with the conclusions of others [1,5,10,12] that its atmospheric lifetime is *ca.* 1000 years.

Acknowledgements We thank Drs H W Jochims, J M Lemaire and F Dulieu for help with the experiments at the Bessy I and SuperAco synchrotron sources, and especially for the 'loan' of beamtime. Finally, we thank Dr C A Mayhew for discussions and a critical reading of the manuscript.

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Figure Captions

Figure 1. Vacuum-UV absorption spectrum of CF_4 recorded at a resolution of 0.08 nm.

Figure 2. Vacuum-UV absorption spectrum of SF_5CF_3 recorded at a resolution of 0.12 nm

Table 1. Thermal electron attachment rate constants, absorption cross-sections at 121.6 nm, and atmospheric lifetimes for CF₄, SF₆ and SF₅CF₃.

Perfluoro compound	k_e (298 K) / cm ³ s ⁻¹	$\sigma_{121.6}$ / cm ²	lifetime / years
CF ₄	$< 10^{-16}$ ^a	$< 8 \times 10^{-22}$ ^b	> 50000 ^{b,c}
SF ₆	2.3×10^{-7} ^{d,e}	1.76×10^{-18} ^b	> 800 ^d
SF ₅ CF ₃	7.7×10^{-8} ^f	1.5×10^{-17} ^g	<i>ca.</i> 1000 ^{f,h}

^a reference 17

^b reference 2

^c reference 18

^d reference 13

^e reference 19

^f reference 10

^g this work

^h reference 12

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Table 2. Energetics of reactions of SF₅CF₃ at 0 K with zero-energy electrons and photons.

Reaction	$\Delta_f H^0 / \text{kJ mol}^{-1}$ (eV)	
	Scheme A ^a	Scheme B ^b
SF ₅ CF ₃ + e ⁻ (0 eV) → SF ₅ ⁻ (-1282) + CF ₃ (-463) ^c (-1621 or -1770)	-124 (-1.29)	+25 (+0.26)
→ CF ₃ ⁻ (-639) + SF ₅ (-915) ^d	+67 (+0.69)	+216 (+2.24)
SF ₅ CF ₃ + hν (10.2 eV) → SF ₅ (-915) + CF ₃ (-463) (-1621 or -1770)	-741 (-7.68)	-592 (-6.14)
→ CF ₃ ⁺ (+409) + SF ₅ ⁻ (-1282)	-236 (-2.45)	-87 (-0.90)
→ SF ₅ ⁺ (+29) + CF ₃ ⁻ (-639)	+27 (+0.28)	+176 (+1.82)

^a Scheme A assumes $\Delta_f H^0$ (SF₅CF₃) = -1621 kJ mol⁻¹ [22].

^b Scheme B assumes $\Delta_f H^0$ (SF₅CF₃) = -1770 kJ mol⁻¹ [3].

^c Reference [24], and assuming the ionisation energy of CF₃ is 9.04 eV [25] and the electron affinity is 1.82 eV [26]. The values in brackets of column 1 are 0 K enthalpies of formation, in units of kJ mol⁻¹.

^d Reference [4], and assuming the ionisation energy of SF₅ is 9.8 eV [3] and the electron affinity is 3.8 eV [27,28]. The values in brackets of column 1 are 0 K enthalpies of formation, in units of kJ mol⁻¹.

Figure 1

vacuum-UV absorption spectrum of CF₄

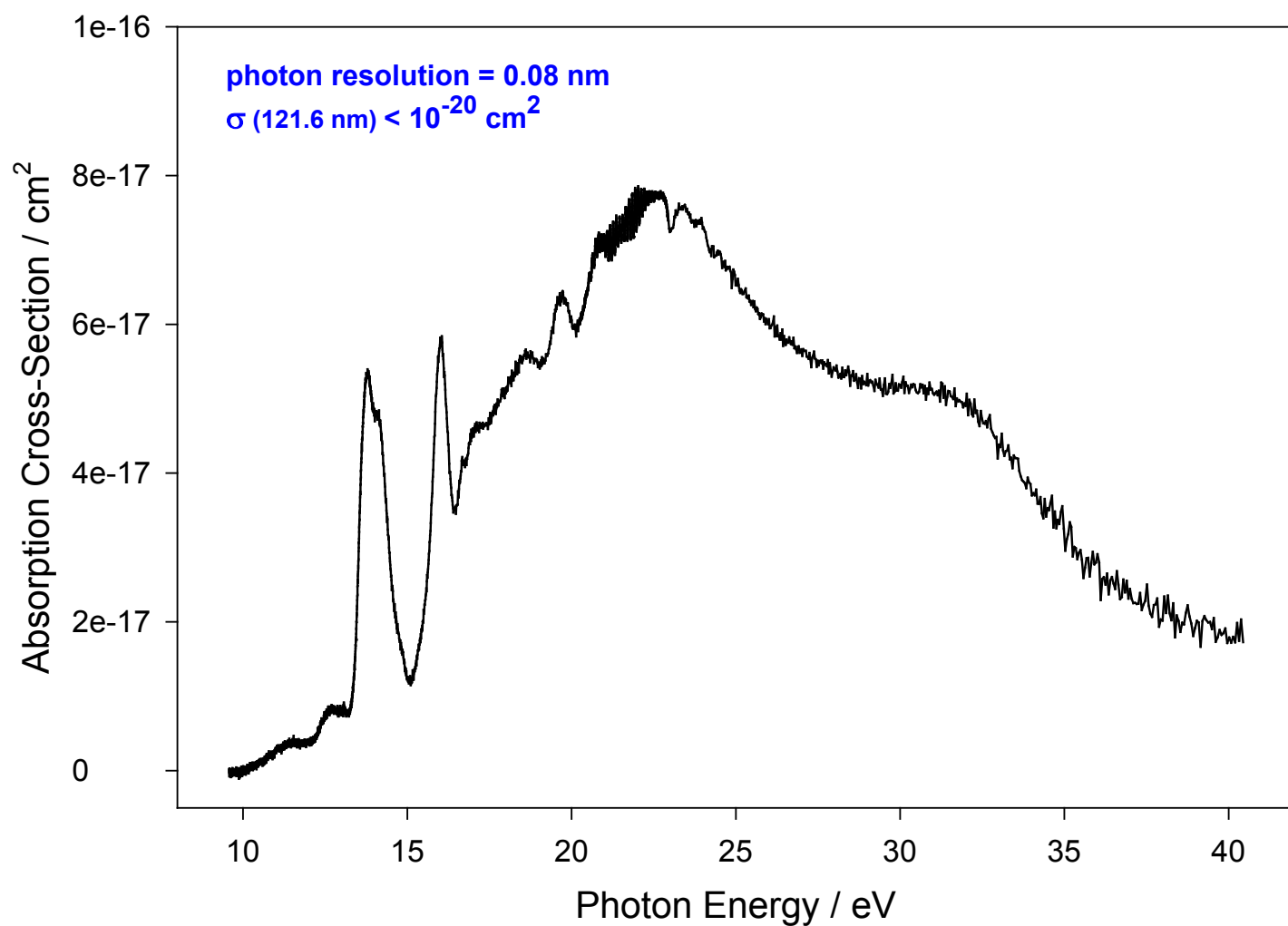
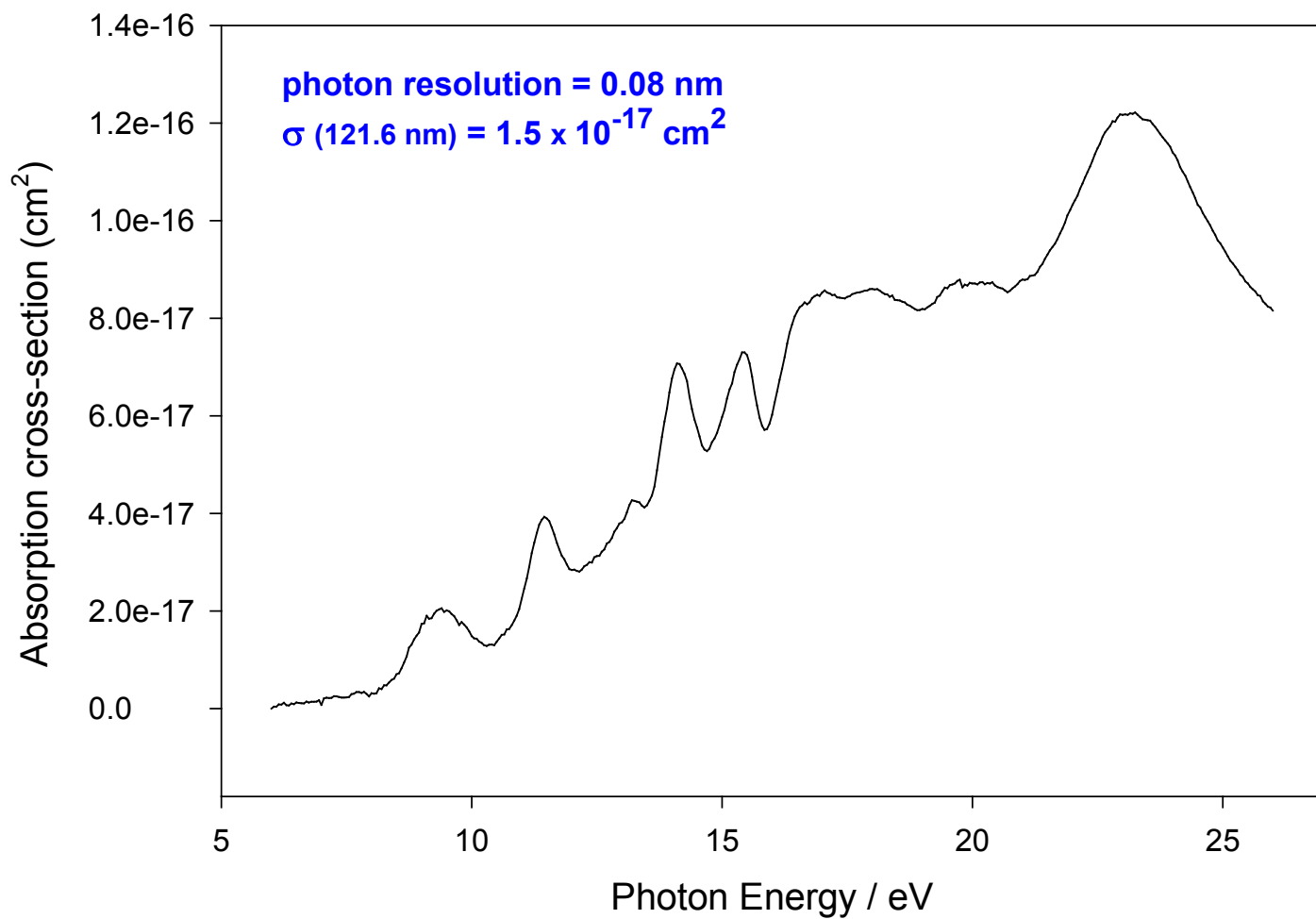


Figure 2

vacuum-UV absorption spectrum of SF₅CF₃



Correction to Table 1 of Chem Phys Letts (2003) 367, 697-703

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The vacuum-UV absorption spectrum of SF₅CF₃

The units of k_e (298 K) and $\sigma_{121.6}$ were given incorrectly in the printed paper. They should be cm³ s⁻¹ and cm², respectively, as shown below.

Perfluoro compound	k_e (298 K) (cm ³ s ⁻¹)	$\sigma_{121.6}$ (cm ²)	lifetime / years
CF ₄	< 10 ⁻¹⁶ ^a	< 8 x 10 ⁻²² ^b	> 50000 ^{b,c}
SF ₆	2.3 x 10 ⁻⁷ ^{d,e}	1.76 x 10 ⁻¹⁸ ^b	> 800 ^d
SF ₅ CF ₃	7.7 x 10 ⁻⁸ ^f	1.5 x 10 ⁻¹⁷ ^g	ca. 1000 ^{f,h}

This was subsequently published in *Chem. Phys. Letts.*, (2003) **369**, 256.