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DOI:

[10.1039/b609314k](https://doi.org/10.1039/b609314k)

Citation for published version (Harvard):

Alvarez Ruiz, J, Kivimäki, A, Stankiewicz, M, Melero García, E, Coreno, M, Ali, S, Koperski, J, Rachlew, E, Vall-Ilosera I Serrano, G, Feyer, V, Tuckett, R & de Simone, M 2006, 'VUV photon induced fluorescence study of SF₅CF₃', *Physical Chemistry Chemical Physics*, vol. 8, no. 44, pp. 5199-5206. <https://doi.org/10.1039/b609314k>

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Vacuum-UV photon induced fluorescence study of SF₅CF₃

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Phys. Chem. Chem. Phys., (2006) **8**, 5199-5206

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DOI : 10.1039/b609314k

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25 above.

Professor Richard Tuckett (University of Birmingham) / July 2011

30 **Vacuum-UV photon induced fluorescence study of SF₅CF₃** [7.9.06]

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45 Receipt/Acceptance Data [DO NOT ALTER/DELETE THIS TEXT]

Publication data [DO NOT ALTER/DELETE THIS TEXT]

DOI: 10.1039/b000000x [DO NOT ALTER/DELETE THIS TEXT]

50 The interaction of SF₅CF₃ with **vacuum-UV** radiation has been investigated by photon induced fluorescence spectroscopy. Total fluorescence yield and dispersed fluorescence spectra of SF₅CF₃ were recorded in the 200-1000 nm fluorescence window. In all cases, the fluorescence spectra resemble those of CF₃X (X=H, F, Cl, and Br) molecules. At photon energies below 20 eV, the emission is attributed to the excited CF₃ and CF₂ fragments. The threshold for the CF₃ emission is **10.2 ± 0.2 eV, giving an upper-limit** estimate for the SF₅-CF₃ bond dissociation energy of 3.9 ± 0.3 eV. The excitation functions of the CF₃ and CF₂ emissions were measured in the photon energy range 13.6 – **27.0 eV**. The resonant structures observed in SF₅CF₃ are attributed to electronic transitions from **valence** to Rydberg orbitals, following similar assignments **in** CF₃X molecules. The photoabsorption spectrum of SF₅CF₃ shows features at the same **energies**, indicating a strong **contribution** from Rydberg excitations.

Introduction

SF₅CF₃ was discovered in the atmosphere **in** 2000 [1] and since then it has been catalogued as a powerful greenhouse effect gas. Entirely of anthropogenic origin [2,3] (so far, the only known source of SF₅CF₃ is connected to the manufacture of fluorochemicals), this molecule shows a global warming potential 18000 times higher than CO₂. Although its concentration in air is still very low, the potential environmental danger of SF₅CF₃ urges the estimation of its impact in the atmosphere. **A** determination of the spectroscopic properties of SF₅CF₃ is **therefore** essential to characterize its behaviour. A brief summary of the main studies devoted to that end and their results are listed below.

70 Photoabsorption investigations [4,5,6,7] have shown that SF₅CF₃ does not absorb visible or UV light below 8 eV. This means that this molecule is not affected by the solar radiation in the lower parts of the atmosphere and only photons in the mesosphere and ionosphere can trigger its photolysis [8]. Studies on its interaction with charged particles has revealed that SF₅CF₃ has a high electron affinity. **Ion-molecule** reactions [9,10,11] and especially electron dissociative attachment [12,13] have been demonstrated to produce the fragmentation of the molecule, **probably being** the main cause of its destruction at altitudes above 50 km. Based on these **results**, scientists have concluded that the lifetime of SF₅CF₃ in the atmosphere is around 1000 years.

80 Important advances in the electronic structure and fragmentation dynamics of this molecule have recently been reviewed [¹⁴], there is still much to be done. By 2001, the threshold photoelectron - photoion coincidence studies of Chim et al. [¹⁵] provided the first ionisation potentials of the molecule but subsequent photoelectron measurements [^{6,7}] reported a richer electronic structure. Only recently have theoretical calculations been able to reproduce well the valence photoelectron spectrum of 85 SF₅CF₃ and give some insight into its photoabsorption spectrum [¹⁶]. Threshold energies of several ions were determined by electron impact experiments [¹⁷], but up to date nothing is known about neutral fragments. Surprisingly enough, it is still unknown whether the molecule dissociates following excitation into its first photoabsorption band.

90 Photon induced fluorescence spectroscopy (PIFS) is a powerful technique for investigating the structure and dynamics of excited molecules. It is especially suitable to trace the production of neutral fragments and to find out the internal energies of the emitting species, thus providing complementary results to those obtained from techniques that detect charged particles. Likewise, the evolution of the fluorescence with excitation energy can also give information about electronic transitions and the 95 dynamics of excited states of the molecule under study.

In this paper we report for the first time the total fluorescence and dispersed fluorescence spectra of SF₅CF₃ following vacuum-UV (VUV) photoexcitation. Apart from these novel data, a high-resolution photoabsorption spectrum is also presented to help the discussion. In order to interpret the spectra, we 100 refer to the theoretical studies on the electronic structure of SF₅CF₃ [^{16,18,19}] but even more substantially to the knowledge of the related SF₆ and CF₃X (X=H, F, Br, and Cl) molecules.

Experimental

105 Experiments were carried out at three different synchrotron radiation laboratories: MAX-Lab (Lund, Sweden), SRS (Daresbury, UK) and Elettra (Trieste, Italy). The photoabsorption spectrum and preliminary total fluorescence yield and dispersed spectra of SF₅CF₃ (not included in the paper) were recorded at the beam line 52 of the MAX I storage ring at the Swedish national synchrotron facility MAX-Lab, in Lund. The beam line, based on a bending magnet, uses a 1-m normal incidence monochromator and provides photons in the VUV range. Due to the low collection efficiency of 110 fluorescence experiments, the slits of the monochromator were fully open (400 μm) during the experiments, giving a resolution of 0.06 eV at hv= 15 eV. The end-station has been described elsewhere [²⁰]. In order to maximise collection of the fluorescence, two optical systems each consisting of a lens and a mirror, are mounted in a cylindrical gas cell inside the experimental chamber. One of the collecting systems directs the light out of the chamber to an external lens that 115 focuses it onto a 0.46-m spectrograph (Jobin-Yvon HR460). The other optical system, perpendicular to the previous one, projects the collected light to a photo multiplier tube (PMT) for un-dispersed, total fluorescence measurements. The PMT (Hamamatsu R647) detects emission in the spectral window of 300-650 nm. The rear part of the station includes a Si photodiode to measure the photon flux of the beam line.

120 Dispersed and un-dispersed fluorescence experiments were also carried out using the new Wadsworth monochromator (station 3.1) of the Synchrotron Radiation Source (SRS) at Daresbury (UK) [²¹]. In brief, the experimental end station consists of two cubical chambers separated by a 3.5 mm diameter aperture. The chamber attached to the end of the beam line is divided into two separate sections by a 3 125 x 10 mm vertical slit, which can be opened or closed by a retractable plate on a vacuum-tight slider. The section in the rear part houses a capillary light guide of length 330 mm and internal diameter 2 mm that couples the synchrotron light to the entrance of the second chamber, where the interaction between the sample and radiation takes place. This arrangement of apertures and glass capillary, plus

two pumping stations used to evacuate the two sections, allows the required differential pumping of ca. **six** orders of magnitude between the interaction region and the monochromator of the beam line. The gaseous sample is admitted laterally in the interaction region *via* a needle valve. The resultant fluorescence is observed at 90° to the incident photon beam by a 0.5 m UV-grade fibre bundle containing 300 fibres attached to a Spectrosil-B window. These fibres display > 50% transmittance in the 250 – 900 nm region, and are connected to the entrance slit of a 0.19-m Jobin-Yvon Triax monochromator. The collected signal is dispersed by either a UV or visible grating turret; each turret contains three gratings with 100, 300 or 1200 grooves mm⁻¹. A 1024 x 256 pixel open-electrode CCD collects the dispersed signal, which uses liquid nitrogen cooling to reduce the dark count level to < 1 count pixel⁻¹ hour⁻¹. **Undispersed fluorescence spectra were** recorded using an uncooled EMI 9883QB photomultiplier tube in place of the fibre optic and the Triax/CCD detection system.

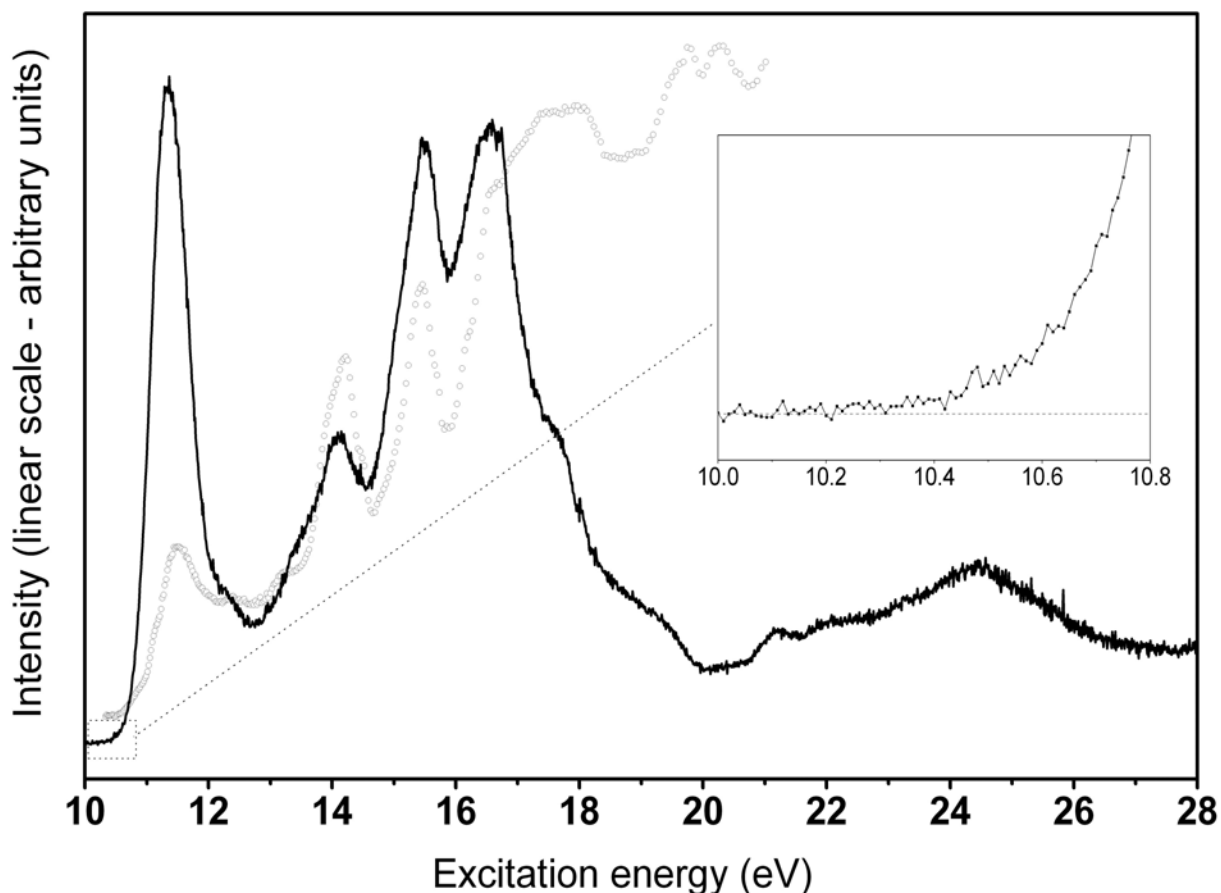
At Elettra, dispersed and un-dispersed fluorescence experiments were performed at the Gas Phase Photoemission beam line, which uses undulator radiation at photon energies from **13–1000 eV**. Exciting radiation is monochomatized by a spherical grating monochromator (five interchangeable gratings are available) equipped with a planar pre-mirror. The incident radiation hits the molecular jet emanating from a hypodermic needle. The fluorescence light emitted into a cone along the electric vector of the incident radiation was collimated with a spherical mirror, **exited** the vacuum chamber through a quartz window, **and** was focused into the entrance slit of the 300-mm Acton fluorescence spectrograph. The light was dispersed by a 1200 lines/mm grating and detected by a nitrogen cooled CCD detector (PRINCETON 10:100B).

The sample gas SF₅CF₃ with a stated purity of 99 % was purchased from Apollo Scientific Ltd and Fluorochem Ltd. It was used without further purification. The energy scales of the spectra are calibrated according to the literature values [⁶]. **None of the dispersed** spectra have been normalized to the wavelength sensitivity of the **different** fluorescence systems, **and this is significant** when comparing **emission** spectra from different **spectrometers**.

Results

Photoabsorption spectrum

The photoabsorption spectrum of SF₅CF₃ was acquired **at MAX-Lab** in the 10-21 eV energy range in steps of 0.25 nm using a Si photodiode. It was obtained by measuring the intensity of the exciting light beam passing through the experimental cell without and with gas and then, by normalizing the ratio of these two current curves to the ring current and pressure fluctuations. **Absolute values of the cross sections are not determined**, since the gas density and the actual interaction length are difficult to estimate. However, the resulting spectrum (Fig. 1) agrees very well with the reported absorption spectra in the literature [⁶, ⁷], revealing the same structures over an increasing background. Because of the contribution of **second-order radiation** from the NIM monochromator output of the beam line **52 at MAX I**, the absorption threshold at 8 eV and the first resonance with the maximum at 9.3 eV could not be recorded.



170 **Fig. 1.** Circles: Photoabsorption spectrum of SF_5CF_3 obtained with a silicon photodiode measured at Max-Lab, beam line 52. Black line: Total
 175 fluorescence yield in the UV-Vis region of SF_5CF_3 measured at Daresbury, beam line 3.1. The insert corresponds to a blow-up of the initial part in the
 total fluorescence yield spectrum. Both spectra have been normalized to the flux of the beam lines.

The lack of theoretical predictions about the excited states of SF_5CF_3 limited the interpretation of its
 175 absorption spectrum in previous studies [6, 7], and the assignment of its different features is still under
 debate. Based on quantum defect analysis, Limão-Vieira et al. [6] assigned all the absorption features
 to Rydberg transitions converging to the first five ionisation potentials. Holland et al. [7] compared the
 absorption spectrum of SF_5CF_3 with those of SF_6 [21] and CF_4 [22], assuming that the structures present
 in the absorption spectra of these two molecules would have their counterparts in the spectrum of
 180 SF_5CF_3 . The valence photoabsorption spectrum of SF_6 is dominated by excitations to unoccupied
 molecular orbitals, while Rydberg transitions have much smaller cross sections [23]. In contrast, the
 photoabsorption features of the CF_3X (X=H, F, Br, and Cl) molecules are most often attributed to
 Rydberg transitions [24, 25, 26]. Holland et al. [7] argued that excitations to molecular orbitals could still
 185 play the main role in the case of CF_4 . Thus they interpreted the photoabsorption spectrum of SF_5CF_3
 in terms of intravalence transitions.

Theoretical calculations of Turki and Einfeld [16] favoured the predominance of Rydberg excitations in
 the region below the first ionization potential (13.96 eV [6]). In particular, the calculated energy for
 the excitation from the highest occupied molecular orbital (HOMO) to the 4s orbital matched very
 190 accurately with the energy of the first absorption feature (11.4 eV) in Fig. 1. The lowest energy
 absorption feature at 9.33 eV was assigned to the HOMO \rightarrow LUMO transition (LUMO = lowest
 unoccupied molecular orbital), as earlier suggested by Chim et al. [15].

195 Total Fluorescence yield

Figure 1 also presents the total fluorescence yield (TFY) of SF₅CF₃ following photoexcitation in the range 10–28 eV from station 3.1 at the SRS in Daresbury. The fluorescence was measured using a PMT which allowed the detection between 190 and 800 nm, approximately. The threshold for fluorescence emission is 10.2 ± 0.2 eV, as shown in the insert of Fig. 1. Several features are observed, the most prominent being centred at the energies 11.4, 14.1, 15.5, 16.6 and 24.5 eV. The three first energies coincide with the peaks in the photoabsorption spectrum, indicating that these excitations lead to fluorescence emission.

Following one of the approaches employed to interpret the photoabsorption spectrum, we analyze the TFY spectrum of SF₅CF₃ by comparing it to those of its constituents. On the one hand, the comparison to SF₅ is straightforward. Recent PIFS investigations of SF₆ have shown that no emission in the 400-1000 nm range occurs below ~30 eV [27], although an early electron-impact induced fluorescence study on SF₆ [28] reported molecular emission around 300 nm for excitation energies above 13.5 eV. We show later that the TFY spectrum of SF₅CF₃ shows no contributions from sulphur-containing species SF_x. On the other hand, CF₃X (X=H, F, Br, and Cl) molecules emit in the ultraviolet and visible when excited with photons above 10 eV and this emission has been extensively studied [29]. The TFY spectra of the CF₃X molecules typically show structures in three regions. Their positions vary slightly depending on the molecule, the first one being at 10-12 eV, the second one around 15 eV and the third one slightly above 20 eV. The structures in the first two regions have been correlated to excitations to different Rydberg states of the molecules. These states are unstable and can dissociate yielding excited CF₃ and/or CF₂ fragments which fluoresce. The features in the total fluorescence spectra at higher energies have a different origin, and they have been interpreted in terms of radiative decay of excited states of the parent ion and of excited CF radicals.

The gross features of the total fluorescence yield of SF₅CF₃ are quite similar to those in the CF₃X molecules, although there is more fine structure in SF₅CF₃ due to the more complicated electronic structure. These similarities in the fluorescence yields strongly suggest that the fluorescence emission of SF₅CF₃ at photon energies between 10-18 eV is due to the CF₃ and CF₂ fragments. However, the TFY spectrum of SF₅CF₃ above 20 eV is less likely attributable to the emission of the parent ion (SF₅CF₃⁺) since this ion has not been observed at all in any mass spectroscopic study [5, 15, 17]. Nevertheless, there exists the possibility that excited states of SF₅CF₃⁺ could fluoresce before dissociation, since mass spectrometry detects ions with lifetimes of the order of microseconds, while fluorescence occurs much faster on a nanosecond timescale.

230 Dispersed fluorescence

The validity of the above assumptions was checked by performing dispersed fluorescence measurements at the most representative excitation energies. At the SRS we used the 0.19 m Triax spectrometer and a UV300 l/mm grating, and Fig. 2 presents the recorded spectra. They have not been normalized to the wavelength sensitivity of the fluorescence collecting system, but as a guideline and according to the manufacturers' specifications, the sensitivity of the spectrometer peaks at ca. 300 nm, reducing to approximately 50% at 200 and 600 nm.

As discussed above, the fluorescence spectrum of SF₅CF₃ could show emission due to the excited CF₃ and CF₂ fragments. In our spectra, there is a broad structure in the 500–800 nm range, similar to the emission band in the CF₃X molecules and attributed to the $\tilde{B}^2A_2'' \rightarrow \tilde{A}^2A_1'$ and $\tilde{C}^2E' \rightarrow \tilde{A}^2A_1'$ transitions in the CF₃ radical [30]. Fig. 2 shows that the maximum of this emission band shifts to lower

wavelengths as the excitation energy increases. This effect has also been observed in CF_3Br and CF_3Cl [31], indicating that higher vibrational levels of CF_3^* (where * indicates an electronically-excited species) are more likely to be populated at larger excitation energies. In the absence of vibrational relaxation, this will produce a shift to lower wavelengths in the observed emission. The fluorescence spectrum measured at the lowest excitation energy (11.3 eV) also shows a weak emission band around 200-250 nm, similarly to the dispersed fluorescence spectra of the CF_3X molecules measured at the photon energies 10-12 eV [29, 31, 32]. The low intensity of this band in SF_5CF_3 may be partly due to decreased detection efficiency in the wavelength range 200-250 nm. This band has also been attributed to the CF_3 fragment and is possibly due to the $\tilde{E}^2A_1' \rightarrow \tilde{X}^2A_2''$ transition [33], although the emitting state may also be a valence state with A_2 symmetry [30]. The upper states of the UV and visible bands should lie very close in energy, since the threshold energies above the CF_3 ground state were found to be practically the same, 6.4 eV, for both emissions [33]. These measurements show that photon absorption in the band with the maximum at 11.4 eV leads to the dissociation of the molecule. At excitation energies of 13.51 eV and higher, an emission band centred around 300 nm is observed in the fluorescence spectra of SF_5CF_3 . The CF_3X molecules typically show an emission band centred at slightly smaller wavelengths (around 280 nm) [29, 34], but it can also peak at 300 nm depending on experimental conditions [32]. This band has been attributed to the $\tilde{A}^1B_1 \rightarrow \tilde{X}^1A_1$ transition in CF_2 . We assign the observed band at 250-350 nm in SF_5CF_3 to this emission.

As mentioned above, the electron-impact induced fluorescence of SF_6 showed emission around 300 nm for electron energies above 13.5 ± 1.5 eV [28]. The emission was tentatively assigned to SF_5 , SF_4 or SF_3 fragments but we believe that it may come directly from SF_6 . (We note that there have been no other observations in the literature of emissions in the UV / visible assigned to SF_x fragments.) In the electron energy loss spectrum of SF_6 [35], there is a peak at 13.3 eV whose energy coincides with the onset of the electron-impact induced fluorescence emission. According to the photoabsorption spectrum of Holland et al [21], this peak corresponds to the $1t_{1g} \rightarrow 6t_{1u}$ transition. The excited SF_6 could undergo fluorescence decay to the lowest $(1t_{1g})^{-1}(6a_{1g})^1$ excited state at around 9.8 eV [35], emitting around the cited wavelength (300-400 nm). Thus, we propose such a mechanism and assign the emission to excited states of the SF_6 molecule. This assignment should be confirmed by ultra-sensitive PIFS studies on SF_6 at those excitation energies. However, any such contribution from the SF_5 component of SF_5CF_3 is ruled out in our SF_5CF_3 spectra because a F atom would need to migrate across the C-S bond, forming electronically-excited SF_6 . This seems unlikely. There is another reason which indicates that the fluorescence observed by Zabbour et al. [new ref 29] is not present in our spectra; the broad shape of the emission band in our high-resolution dispersed spectrum (Fig. 4) differs significantly from the emission observed in the electron-impact induced fluorescence of the SF_6 molecule. At excitation energies above 19.2 eV, a weak emission feature develops around 400 nm, most likely due to $\text{N}_2^+ B^2\Sigma_u^+ (v'=0) - X^2\Sigma_g^+ (v''=0)$ emission from a small N_2 impurity (see below).

Finally, we discuss the possibility of other emitters being responsible for the bands observed in the dispersed fluorescence spectra of SF_5CF_3 . The CF radical has two known emission systems: $A^2\Sigma^+ - X^2\Pi$ and $B^2\Delta - X^2\Pi$ with emission wavelengths in the wavelength regions 223-256 nm and 197-220 nm, respectively [36]. These systems, particularly the former one, could in principle contribute to the observed spectra. However, the creation of the CF fragment from the SF_5CF_3 molecule would require the breaking of three bonds, needing an energy of approximately 12.7 eV [new ref 38]. Since the excitation energy of the CF radical in the $A^2\Sigma^+$ state is 5.29 eV [37], the CF fragment should not give any contribution to fluorescence emission at excitation energies below ca. 18 eV. Fluorescence could also take place between the excited states of the neutral and/or ionic SF_5CF_3 molecule itself, but if present in our spectra we could not identify them.

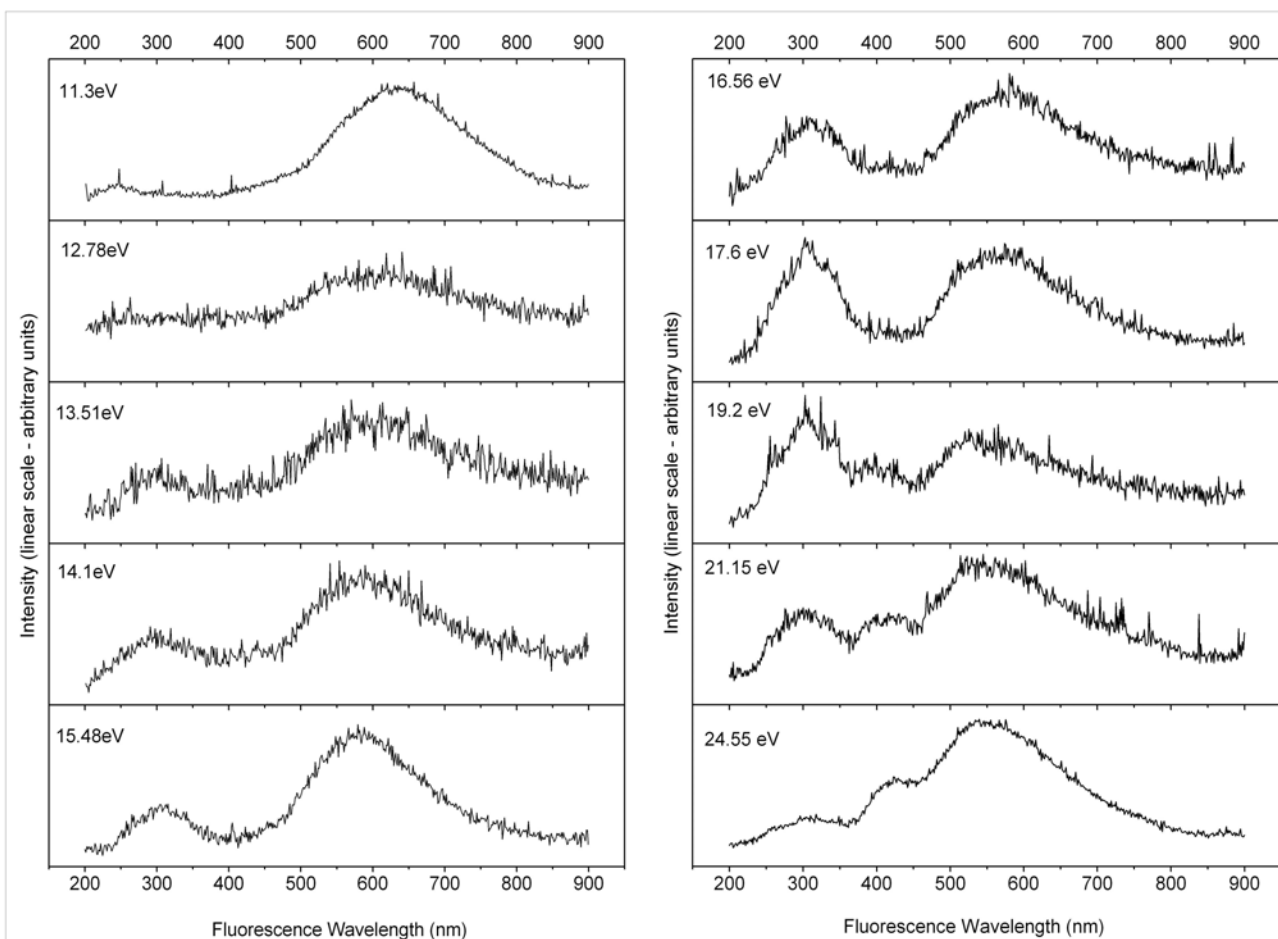


Fig. 2. Dispersed fluorescence spectra of SF_3CF_3 at ten different excitation energies. Data taken using station 3.1 at the Daresbury SRS.

The higher flux of the Gas Phase beam line and the better spectral resolution of the spectrometer at Elettra allowed us to investigate the intensity behaviour of the CF_3 and CF_2 fluorescence with excitation energy. Two fluorescence regions, one from 550 to 650 nm (CF_3 emission) and the other from 250 to 310 nm (CF_2 emission), were selected and measured in the photon energy range 13.6 – 27.0 eV in steps of 0.1 eV. Fig. 3 presents both excitation functions together with a total fluorescence yield obtained with the Elettra fluorescence spectrograph working in zero order. The difference in the relative intensities of the peaks in the TFY obtained at Elettra from those measured at Daresbury (Fig. 1) is explained by the difference in the quantum efficiency of the detectors; the CCD spectrograph at Elettra is more sensitive to visible light than the EMI 9883 QB photomultiplier tube used at Daresbury. The fluorescence around 550 nm follows the profile of the TFY, whereas the fluorescence of region 280 nm resembles more that of the TFY from Daresbury. Both excitation functions reveal the same structures but with different relative intensities. However, the two partial fluorescence yields peak at slightly different energies in the interval 15.0-16.0 eV. This may be caused by two different excited states of SF_3CF_3 being responsible for dissociation to the emitting states of CF_3 and CF_2 .

Higher-resolution dispersed fluorescence spectra were also recorded at the Gas Phase Beam line using the 300-mm ACTON fluorescence spectrometer with a 1200 lines/mm grating. The wavelength range 200-1000 nm was measured in several 70 nm windows, and the final spectrum was obtained by joining them together (Fig. 4). At an excitation energy of 16.5 eV, the spectrum is very similar to that obtained at Daresbury (Fig. 2), showing fluorescence due to the CF_3 and CF_2 fragments. At 24.5 eV,

the larger number of rulings per mm of the grating allow us to resolve the narrow bands at 390 nm and 427 nm that are due to the $B - X$ transitions in the N_2^+ molecular ion. Despite the low amount of the N_2 impurity (~1%) in the sample, these emission bands are intense due to the high photoionization cross section of the N_2^+ $B^2\Sigma_u^+$ state just above its threshold. The fluorescence spectrum taken at a photon energy of 46 eV reveals numerous sharp lines. The most intense of them in the range 650-750 nm and around 920 nm can be assigned to transitions in neutral F and S atoms, respectively^[38]. Some fluorine lines are also visible in the spectrum measured at 16.5 eV photon energy, but they must be caused by higher-order radiation from the beamline monochromator, since the upper states of these transitions have at least 14.5 eV of internal energy^[38]. Therefore, the excitation functions of the fluorine lines at 731.1 and 739.9 nm, shown in Fig. 6, should be inspected with caution (see Discussion). The dispersed fluorescence spectrum at 46 eV also shows molecular-like bands around 420 nm and 500 nm, but the signal-to-noise ratio of the spectrum is insufficient to identify the species responsible for these emissions. However, it is likely that fluorescence from the CF_3 radical may still account for the band at 500 nm.

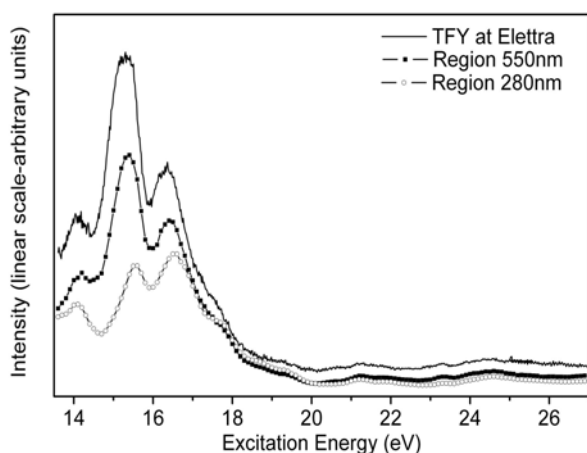


Fig. 3. Excitation functions of fluorescence regions 250–310 and 550–650 nm, and the total fluorescence yield of SF_5CF_3 measured at Elettra. The spectra have been normalized to the flux of the beamline.

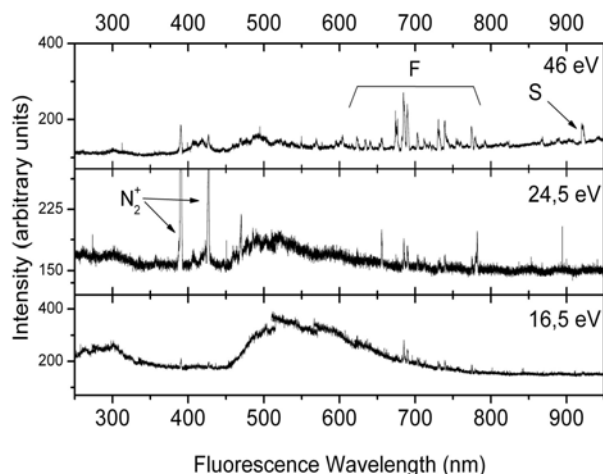


Fig.4. Dispersed fluorescence spectra of SF_5CF_3 measured at Elettra. The abnormal shape of the fluorescence spectrum for wavelengths around 500-600 nm at 16.5 eV is due to the quantum efficiency of the detector at these wavelengths.

335

Discussion

The identification of the CF_3 fragment as responsible for the fluorescence emission in SF_5CF_3 at the lowest photon energies allows us to conclude that photon absorption within the band which has a

340 maximum at 11.4 eV can lead to dissociation of the molecule. Furthermore, we can estimate the energy needed to break the SF₅–CF₃ bond. In the CF₃X molecules, the emission observed at 10–12 eV excitation energy was attributed to the excited states lying about 6.4 eV above the ground state of the CF₃ fragment [33]. This corresponds to the dissociation CF₃X → CF₃* + X. For SF₅CF₃, the lowest energy to produce a CF₃ fragment is that for the reaction SF₅CF₃ → CF₃ + SF₅. So if we begin to
345 observe the excited CF₃ fragment at 10.2 ± 0.2 eV (Fig. 1) and the internal energy of the CF₃* fragment is 6.4 eV, we determine an upper limit for the SF₅–CF₃ bond dissociation energy of 3.8 ± 0.2 eV. This value, however, is subject to some uncertainties. Firstly, the excitation energy of the CF₃ fragment determined in ref. 34 relies on the correct vibrational numbering of the discrete CF₃ emission spectrum [new ref 33]. If this numbering is indeed correct, then the internal energy should actually be
350 6.29 eV, which increases the value for the bond dissociation energy to 3.9 ± 0.3 eV. Secondly, it is possible that in this study by Suto and Wahida [new ref 33] either or both electronically-excited CF₃ and ground-state SF₅ fragments are not formed in their lowest vibrational state. In that case, the determined SF₅–CF₃ bond dissociation energy would be too high. Our result yields a slightly lower value than, but within error limits, for the SF₅–CF₃ bond dissociation energy from that determined by
355 threshold photoelectron – photoion coincidence spectroscopy, 4.06 ± 0.45 eV [5]. The calculated SF₅–CF₃ bond dissociation energy is slightly lower, 3.50 eV [13].

In the CF₃X molecules, the appearance energy for the CF₂ emission is 2.02 eV higher than for the CF₃ emission [34]. This corresponds to the dissociation CF₃X → CF₂* + X + F. In SF₅CF₃ the appearance
360 energy for CF₂ emission should be around 12.2 eV (= 10.2 eV + 2.02 eV). Unfortunately, partial fluorescence measurements could not be done across this threshold. The measurements of Fig. 3 show that the CF₂ emission is already intense at 13.6 eV, although we note that this band is not visible with the excitation energy of 12.78 eV in Fig. 2.

365 The CF₂ and CF₃ fluorescence yields have intensity maxima at the same energies as the peaks in the photoabsorption spectrum. This observation indicates that excited states of SF₅CF₃ dissociate along potential energy curves that yield excited CF₃ (which either emits light or further dissociates into excited CF₂). A similar behaviour has also been observed in the fragmentation of the ground and excited states of SF₅CF₃⁺ [14]. The parent ion preferentially dissociates to CF₃⁺ + SF₅ and not to SF₅⁺ +
370 CF₃, as can be concluded from the CF₃⁺ ion yield which mirrors the threshold photoelectron spectrum of SF₅CF₃ [15]. Such a property is typical of small molecules, dissociating only on one repulsive potential energy surface with no curve crossing. It appears that SF₅CF₃ can behave as a pseudo-diatomic molecule, with a much lower density of vibronic states that it actually possesses. Fluorescence is just one of many decay channels for excited states of the parent molecule and therefore
375 the absorption spectrum probably contains much intensity due to excitations that are “dark” to radiative decay; for example, dissociation to ground-state CF₃ and electronically-excited SF₅ will not be observed in these experiments, because SF₅ does not emit in the UV / visible. However, the similar trend of fluorescence yield and the absorption spectrum strongly suggests that excitations on SF₅CF₃ have an important molecular CF₃ character. It should be noted that absolute values of fluorescence
380 quantum yields are not determined in these experiments.

As already described, the fluorescence emission up to around 16 eV in the CF₃X molecules has been attributed to Rydberg excited states of the parent molecule [29]. In SF₅CF₃, the corresponding region in the total fluorescence yield can extend up to 18 eV (up to this energy the CF₃ emission stays intense).
385 Based on this reasoning, we attempt to assign the features in the TFY to Rydberg excitations. The energies of the Rydberg excitations converging to the ionization energies of the valence orbitals can be estimated using the calculated term values of Turki and Eisfeld [16] and the ionization energies

reported by Holland et al [7]. As the number of possible Rydberg excitations is large, the energies of some will inevitably coincide with experimental values. Therefore, we consider only transitions to the lowest Rydberg 4s and 4p orbitals, which according to the calculations can be expected to have the highest oscillator strengths [16]. The results are shown in Fig. 5 where the possible Rydberg transitions are displayed with bars (the heights of the bars are arbitrary). Obviously, definite assignments for the features cannot be given by the energy basis only. However, it seems that transitions to the 4s Rydberg orbital could account for the most intense features in the TFY. The TFY peak at 11.4 eV shows a rather clear shoulder at 12.3 eV that can be due to the excitation to the 4p orbital, as calculated in [16]. We note that the Rydberg orbitals of d type were not taken into account in the calculations of ref. 16. In the CF₃X molecules, such excitations have also been suggested to be responsible for fluorescence emission [29].

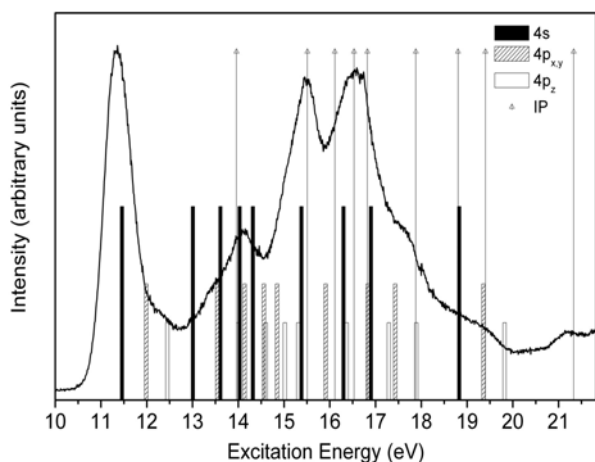


Fig. 5. The solid curve displays the TFY measured at Daresbury (taken from Fig. 1). The bars show the estimated positions of Rydberg transitions (the heights of the bars are arbitrary), while thin arrowed lines present the ionisation energies of the different valence orbitals as reported by Holland et al [7].

At higher excitation energies, excited ionic fragment CF₃⁺ could, in principle, start to emit around 20 eV, but it was not found to contribute significantly to the observed fluorescence in the CF₃X molecules [34]. Thus, the intensity in the TFY spectrum (Fig. 1) could still be caused mostly by the CF₃ and CF₂ fragments. The partial fluorescence measurements of Fig. 3 reveal that there is fluorescence intensity in the corresponding wavelength regions. No other emitters, apart from N₂⁺, have been identified in the dispersed spectra. In particular, no evidence of emission from the parent molecular ion, SF₅CF₃⁺, has been encountered, in contrast to the CF₃X molecules where CF₄⁺, CF₃Cl⁺ and CF₃H⁺ all show radiative decay from electronically-excited states [new ref 30].

Atomic emission due to excited fluorine fragments could begin around 17.8 eV. The upper limit for the dissociation SF₅CF₃ → SF₄CF₃ + F has been estimated to be 3.4 eV [13] and the excited F atoms, which fluoresce in the visible or near infra red, have internal energies of 14.37 eV or more [38]. This energy occurs in the photon energy range where the second order radiation gives a strong contribution to the excitation function (Fig. 6) which, added to the presence of the molecular emission background, masks any onset of a new emission. However, the excitation functions of the fluorine transitions at 731.1 and 739.9 nm, due to the 2p⁴(³P)3p(²S) → 2p⁴(³P)3s(²P) and 2p⁴(³P)3p(⁴P) → 2p⁴(³P)3s(⁴P) transitions respectively [38], show some features at different excitation energies. The most prominent one begins at around 20.5 eV and we tentatively assign it to the fluorine production channel SF₅CF₃ → SF₅^{*} + CF₃ → SF₄ + F^{*} + CF₃. This process requires an energy of 20.2 eV (= 5.84 + 14.37 eV), where the former energy has been calculated using the enthalpies of formation given in ref. 38 and the latter value is the internal energy of the F atom. This energy coincides quite well with the onset of the

resonance. The rest of the features around 19, 23 and 24.5 eV are weak enough to be considered
 425 ambiguous but still worth noting as possible different dissociation limits that produce excited **F atoms**.

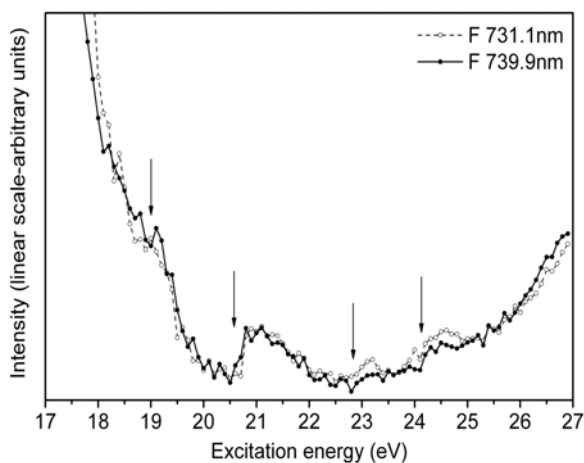


Fig. 6. Excitation function of F 731.1 (dashed line) and 739.9 nm (continuous line) atomic transitions recorded after excitation of SF₅CF₃ with 17-27 eV photons. The arrows indicate the appearance threshold of the resonances discussed in the text.

430 The dispersed fluorescence spectrum (Fig. 4) shows that at 24.5 eV excitation energy the total intensity of the atomic fragment lines is far lower than that of the molecular fragments. Atomic emission becomes proportionally more important at higher photon energies, as evidenced by the spectrum excited with 46 eV photons. At this excitation energy, a fluorescence feature at 922 nm can be attributed to the 3p³(⁴S)4p(⁵P)→3p³(⁴S)4s(⁵S) transitions in neutral sulphur atoms [³⁸]. The same
 435 transitions in the SF₆ molecule were observed to have a resonant behaviour in the photon energy range 32-50 eV [²⁷]. From the energy considerations, the emission was concluded to follow from the neutral dissociation of SF₆. The same effect could occur also in SF₅CF₃, this time resulting from an excitation in the SF₅ side of the molecule.

440 Conclusions

Photon induced fluorescence experiments have been performed for the SF₅CF₃ molecule in the **vacuum-UV** excitation energy range. The total fluorescence yield and dispersed fluorescence spectra of SF₅CF₃ resemble those of the CF₃X (X=H, F, Cl, and Br) molecules, **showing** molecular bands due to the excited CF₃ and CF₂ fragments at similar excitation energies. The emission due to the excited
 445 CF₃ fragment **has a threshold of 10.2 ± 0.2 eV, leading to an upper-limit estimate of the SF₅-CF₃ bond dissociation energy of 3.9 ± 0.3 eV**. The CF₃ and CF₂ emissions are most likely **caused** by excitations of electrons from valence orbitals into Rydberg orbitals in the CF₃ side of the molecule. Thus, we proposed a partial explanation of the total fluorescence yield spectrum in terms of those Rydberg transitions. The photoabsorption spectrum shows peaks at the same energies as the total and partial
 450 fluorescence yields, implying the same origin for these features. However, the photoabsorption spectrum obviously displays other structures also due to intravalence transitions (especially in the SF₅ side), which will not be followed by fluorescence decay.

The emission due to the CF₃ and CF₂ fragments is an important contributor to the total fluorescence in the 200-1000 nm range also at photon energies above 20 eV. Fluorescence emission due to ionic
 455 molecular fragments is **negligibly weak**, while fluorescence in atomic fragments, especially in fluorine atoms, becomes proportionally more intense between 25 and 46 eV photon energy. The fluorescence emission of SF₅CF₃ provides one more hint that the structural parts (SF₅ and CF₃) of this molecule **behave** independently.

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Acknowledgements

The authors are indebted to Dr. Bonifacio de Andres for his institutional support and Dr. Oscar Rubio for his help in the theoretical discussions. Financial support from the Göran Gustafsson Foundation, from the Swedish Research Council (VR), from the European Community - Research Infrastructure Action under the FP6 "Structuring the European Research Area" Programme (through the Integrated Infrastructure Initiative "Integrating Activity on Synchrotron and Free Electron Laser Science"), and from EPSRC UK are gratefully acknowledged.

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