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An experimental study of SF_5CF_3 by electron energy loss spectroscopy, VUV photo-absorption and photoelectron spectroscopy

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We dedicate this paper to Professor Tilmann Märk, not only a renowned scientist but also a loyal colleague
and trusted friend, on the occasion of his 60th birthday.

Abstract

A comprehensive study of the spectroscopy of trifluoromethyl sulphur pentafluoride, SF_5CF_3 is reported. A high resolution VUV photo-absorption spectrum of SF_5CF_3, has been measured using synchrotron radiation in the range of 5.5–10.8 eV ($225 > \lambda > 115$ nm) and compared with electron energy loss spectroscopy. Excited states are reported in the 8.5–22.5 eV region. Ionic states are probed by HeI photoelectron spectroscopy. The photolysis of the compound has also been investigated to give an estimate of the lifetime in the atmosphere. It is estimated that the atmospheric lifetime of SF_5CF_3 is of the order of 1000 years; the calculated global warming potential (GWP) is found to be 18,500.

Keywords: VUV photo-absorption; Spectroscopy; Synchrotron radiation; Photolysis rate; EELS; Photoelectron spectroscopy

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1. Introduction

SF_5CF_3 has only recently been detected in the terrestrial atmosphere [1] and identified as a potent greenhouse gas. Although its origins are still unclear SF_5CF_3 is believed to be purely anthropogenic in origin, probably being related to the plasma technology industry and gas dielectrics. The spectroscopy, dissociation dynamics and chemical reactivity of this compound are still poorly understood having only been the subject of research in the last two years. The first experimental measurements reported for this molecule concentrated upon its infrared properties. Sturges et al. [1] measured the room temperature IR photo-absorption cross sections and compared them to preliminary data reported by Eggers et al. [2], subsequently refined and discussed by Griffiths [3]. The IR spectra have been recently re-measured over a wave number range of 100–4000 cm^{-1} with spectral resolutions of 0.01 and 0.90 cm^{-1} [4] while the temperature dependence of the cross section was extensively studied between 203 and 298 K over the range 600–1500 cm^{-1} with a 0.03 cm^{-1} resolution [5].

There has been much speculation as to the mechanisms by which SF_5–CF_3 is destroyed in the terrestrial atmosphere with current suggestions including: (i) UV photo-dissociation in the stratosphere and mesosphere and (ii) by electron attachment and ion–molecule reactions in the mesosphere. Experiments have also been performed to determine the ionisation and fragmentation of trifluoromethyl sulphur pentafluoride using threshold photoelectron photoion coincidence (TPEPICO) spectroscopy [6]. Chim et al. [6] measured the fragmentation of the valence states of SF_5–$CF_3{}^+$ over energy range of 12–26 eV by means of

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VUV synchrotron radiation and reported the appearance energies of fragment ions. The role of bimolecular reactions with positive ions inherent in the upper atmosphere has been investigated to obtain rate coefficients and product ion distributions for the related reactions [7–9]. A comprehensive study of the electron attachment rate constant has been performed by Kennedy and Mayhew [10] and compared to low energy electron attachment at a high incident electron resolution by mass spectrometry [11]. Electron impact ionisation cross sections close to threshold have been reported [12] and the role of SF_5CF_3 in the terrestrial atmosphere have been evaluated.

In this paper we report a high resolution VUV photo-absorption spectrum. The first pseudo-photo-absorption spectrum of SF_5CF_3 in the energy range 6–22 eV was measured by Kendall and Mason [13] and has since been compared with photo-absorption cross sections measured in the VUV region by Chim et al. [14] and by Limão-Vieira et al. [15]. In addition, the HeI photoelectron spectrum recorded with a higher resolution than the TPEPICO spectrum provides the ionisation energies of the molecule in an energy range up to 20 eV.

2. Experimental apparatus

2.1. The photo-absorption spectrum

The high resolution VUV photo-absorption spectrum was recorded at the ultraviolet vacuum line (UV1) synchrotron radiation of the Astrid Facility at Aarhus University, Denmark [16]. The set-up used has been described in detail in an earlier publication [17] so only a brief description is given here. The UV beam passes through a simple static gas cell with an absorption path length of 25 cm and the transmitted intensity, I_t measured at 0.05 nm intervals using a photomultiplier detector. The transmitted light intensity, as well as, the sample pressure (measured on an MKS 390HA Baratron capacitance manometer, ±0.1%) and the synchrotron beam ring current were monitored at each wavelength. The typical resolution was ~0.075 nm. The sample cell is then evacuated and the radiation transmitted through the empty cell I_0 is recorded. The absolute photo-absorption cross section was calculated using the attenuation Beer–Lambert law:

$$I = I_0 \exp(-n\sigma x) \tag{1}$$

with n is the target gas number density, σ is the absorption cross section, and x is the path length [18]. Absolute photo-absorption cross sections have been obtained with accuracy estimated to be around 5%. The minimum wavelength achieved is determined by the entrance and exit windows in the gas cell, in the present case, a LiF entrance window and a CaF_2 exit window in front of the photomultiplier tube were used such that the lowest wavelength at which reliable data could be collected was ~115 nm. The cross section was measured over a wide range of pressures (0.075–0.750 Torr) to ensure that the data was free from any saturation effects [19] with typical attenuations of less than 10%. Care was also taken to avoid any second-order light effects in these experiments. The SF_5CF_3 gas was purchased from Argo International Ltd. with a stated purity of 99.9%. We detected a small (0.04%) CS_2 contamination.

2.2. Electron energy loss spectrum

The electron energy loss spectrometer used for studying the SF_5CF_3 molecule has been described in detail elsewhere [13,20]. Briefly, the thermionically emitted electrons are energy selected in a hemispherical energy selector, providing electrons with a resolution of ~50 meV. The electron beam collides at right angle with the effusive molecular target, and the scattered electrons are focused and energy analysed in a second hemispherical analyser with an acceptance entrance angle ~1°, before detection using a continuous dynode electron multiplier. The analyser can rotate around the scattering centre covering an angular range (θ) from -10 to 130° with respect to the incident electron beam. The angular resolution is ±1.5°. electron energy loss spectroscopy (EELS) provides an alternative methodology for probing the excited states of a molecule, since at large scattering angles and low incident electron energies forbidden transitions are dominant but at small scattering angles and high incident energies (T), allowed transitions are dominant [20]. If the EEL spectrum is recorded at incident energies (T) in excess of 100 eV and at scattering angle (θ) $\sim 0°$, this spectrum may be directly compared with a photo-absorption cross section. We therefore have used this technique to explore the photo-absorption of SF_5CF_3 in the 6–22 eV energy range.

It is possible to relate the energy loss spectrum to the differential oscillator strength and then to the optical absorption cross section if the spectrum is recorded at $\theta \approx 0°$ and high incident electron energy ($T = 100$ eV) such that the electron energy loss E is much smaller than T. The inelastic scattered intensity is converted to a relative differential oscillator strength distribution, df/dE [21]. Then,

$$\frac{\mathrm{d}f}{\mathrm{d}E} \propto \frac{E\Delta\theta}{R} \frac{1}{\ln\left[1 + (\Delta\theta/\gamma)^2\right]} I(E) \tag{2}$$

where $\gamma = (E^2/(4T(T - E))$, d$f$/d$E$ is the differential oscillator strength distribution, $\Delta\theta$ is the acceptance angle, R is the Rydberg constant and $I(E)$ is the scattered intensity of the electron beam.

The EELS data must be normalised to a known cross section at a particular wavelength measured in the optical experiment in order to obtain absolute values. The cross section may then be calculated from:

$$\sigma_{\mathrm{pa}} = 109.75 \frac{\mathrm{d}f}{\mathrm{d}E}$$

where σ_{pa} is the photo-absorption cross section in Mbarn and df/dE is in eV^{-1}. The present EEL spectrum has been scaled to the photo-absorption spectrum at 9.336 eV.

2.3. Photoelectron spectrum

The HeI (21.22 eV) photoelectron spectrum of SF_5CF_3 was recorded at the Université de Liège, Belgium. The apparatus has been described in detail previously [22]. Briefly, the spectrometer consists of a 180° cylindrical electrostatic analyser with a mean radius of 5 cm. The analyser is used in constant energy pass mode. The incident photons are produced by a dc discharge in a two-stage differentially pumped lamp. The energy scale is calibrated using xenon ($^2P_{3/2} = 12.130$ eV and $^2P_{1/2} = 13.436$ eV) [23] and resolution of the present spectrum is measured from the full width half maximum of the Xe peaks to be 22 meV, in presence of SF_5CF_3.

3. Results and discussion

3.1. Spectroscopy of SF_5CF_3

The VUV photo-absorption cross section spectrum for SF_5CF_3 is shown in Fig. 1 and compared to a photo-absorption cross section derived from electron energy loss spectra in Fig. 2. There is good agreement in the shape and magnitude of the cross sections recorded by the two methods. The spectrum is composed of a rather intense absorption band centred at 9.336 eV with a local maximum cross section of 17.078 Mb (Figs. 1 and 2). The feature close to 11.0 eV is only partially recorded due to the cut-off in the transmission of the CaF_2 window. As noted by previous authors [13–15], there is no evidence for vibrational features in any of the absorption bands. CS_2 contamination of 0.04% is established by the presence of structure below 8 eV [24] and had to be removed from the present spectrum. This contamination is responsible for a minor band centred at 6 eV, very weak features at 6.823 eV and around 7 eV and weak features at 7.57, 7.698 eV and a less weak feature at 7.783 eV. However, these do not affect the magnitude of the SF_5CF_3 absorption cross section at least to within the estimated ±5% error.

Assignment of the valence states of SF_5CF_3 is complicated since there is still no agreement as to the symmetry type for this molecule, either C_{4v} (a_1, a_2, b_1, b_2, e) or C_s (a', a'') [3,25]. Griffiths [3] concluded from his infrared and Raman spectra that the barrier to internal rotation is low or zero, and according to the observed patterns, classified the molecule symmetry as being C_{4v}. However, recent calculations have shown that the internal barrier to rotation and the internal torsion C–S mode have values at about 6.45 cm^{-1} (77 J mol^{-1}) and 15 cm^{-1}, respectively [25], the latter being of the same order of magnitude of the energy necessary to overcome the barrier, suggesting the symmetry of SF_5CF_3 to be C_s. Nevertheless, both symmetry types can be related to the irreducible representations and in C_s notation both b_2 and a_2 correlate with a'', a_1 and b_1 correlate with a', and e to the crossed product of a' and a'' [26]. Therefore, the 24 vibrational distinct modes are classified in the C_s symmetry as $\Gamma_{vib} = 15A'' + 9A''$ with their fundamental energies summarised by Ball [25].

We have fitted the HeI photoelectron spectrum with a series of Gaussian curves (Fig. 3) in order to determine the most probable values of the ionisation energies and found the

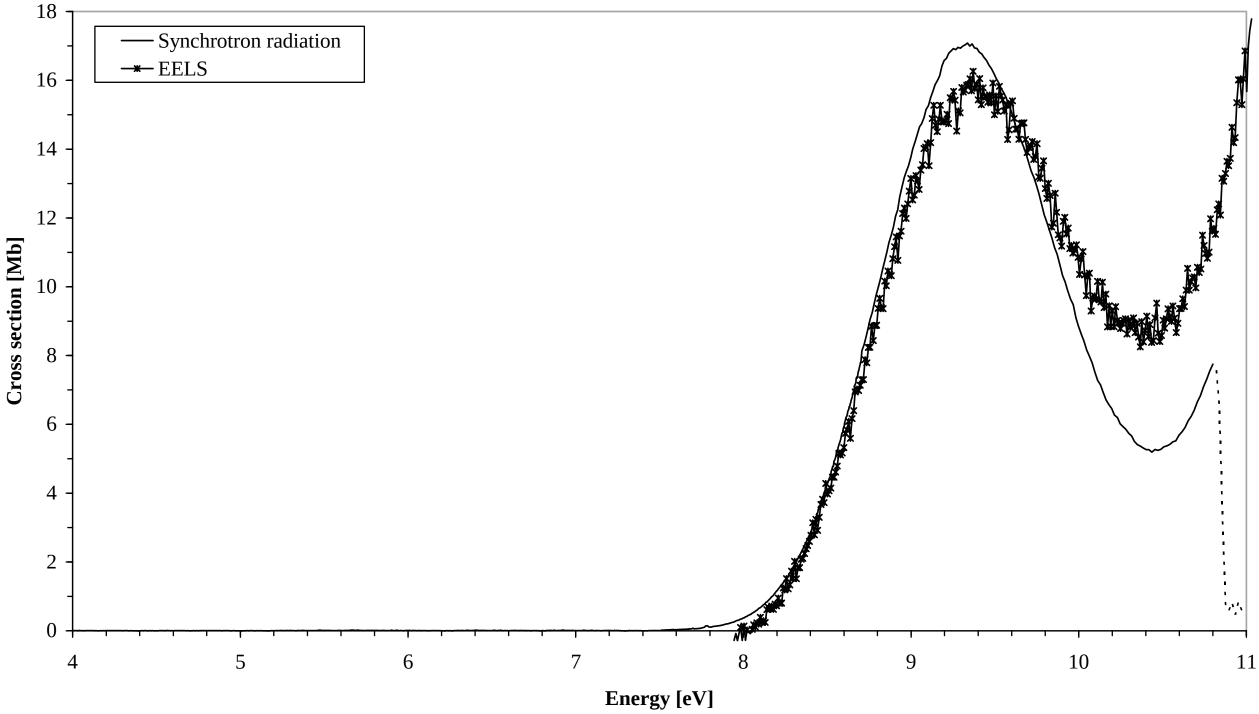

Fig. 1. The high-resolution photo-absorption spectrum of SF_5CF_3 recorded at the ASTRID synchrotron ring facility.

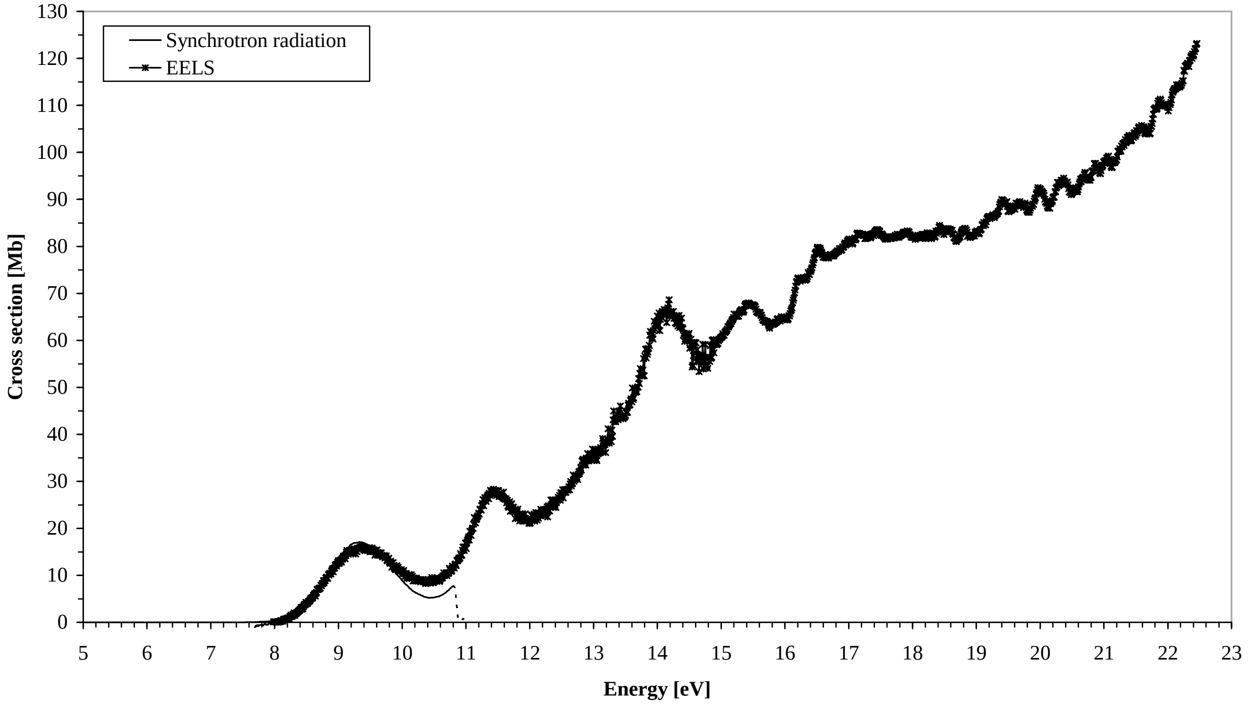

Fig. 2. The photo-absorption cross section derived from EELS measurements compared to those collected using the ASTRID synchrotron ring facility.

following values: 13.960, 14.699, 15.632, 16.147, 16.461, 16.845, 17.199, 17.894, 18.721 and 19.365 eV. The photoelectron is rather similar to the threshold photoelectron spectrum [6] but with the bands being much better resolved.

Special attention has been devoted to VUV photo-dissociation studies of SF_5CF_3 because excitation in the energy region below the first ionisation potential, results in prompt dissociation along the S–C bond due to the repulsive nature of the σ^* excited states [6]. Therefore, the low-lying valence excited states should arise from excitations of the σ HOMO to the σ^* LUMO, a transition involving valence shell type orbital in the S–C bond.

Structures observed for energies above 8 eV from the EEL spectrum (Fig. 2), have been tentatively assigned to members of Rydberg series converging to the ionisation energies (Table 1), despite diffuseness. The peaks position, E_n, must fit the Rydberg formula: $E_n = E_\mathrm{i} - R/(n - \delta)^2$, where E_i are the ionisation energies, n is the principal quantum number of the Rydberg orbital of energy E_n, R is the Rydberg constant and δ is the quantum defect.

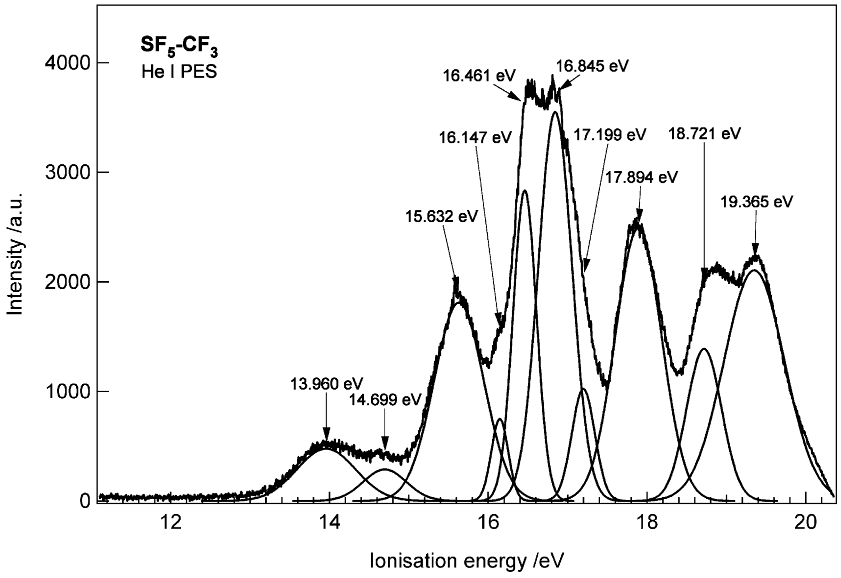

Fig. 3. The HeI photoelectron spectrum of trifluoromethyl sulphur pentafluoride. A series of Gaussian curves have been fitted to the data (see text details).

Table 1
Energy values, quantum defect (δ) and assignment of the Rydberg series converging to the ionisation energies (IE) (energies in eV)

Energy	Quantum defect	Assignment
IE = 13.960 eV		
9.336	2.28	4s
(12.420)	2.03	5s
12.984	2.27	6s
11.431	1.68	4p
(12.740)	1.66	5p
(13.228)	1.69	6p
IE = 14.699 eV		
11.431	0.96	3d
13.228 (?)	0.96	4d
IE = 15.632 eV		
(12.359)	1.94	4s
14.185	1.93	5s
IE = 16.461 eV		
12.984	2.02	4s
(14.878)	2.07	5s
IE = 16.845 eV		
(13.443)	2.00	4s
15.425	1.90	5s
15.943	2.12	6s

Values in parentheses indicate features not well resolved. See text.

Table 2
Ionisation energies (eV) observed in the HeI and in the TPE spectra of SF_5CF_3 (vertical values, in eV)

He(I) PES (this work)	TPES[a]
13.960 ± 0.011	14.13
14.699 ± 0.011	–
15.632 ± 0.001	15.68
16.147 ± 0.004	–
16.461 ± 0.005	–
16.845 ± 0.003	16.94
17.199 ± 0.013	–
17.894 ± 0.001	17.86
18.721 ± 0.001	–
19.365 ± 0.003	19.44
Out of range	21.34
Out of range	22.01
Out of range	24.67

[a] Ref. [6].

The feature at 9.336 eV has been tentatively assigned to the $n = 4$ member of a Rydberg series converging to the 13.960 eV ionisation limit (Table 1). The quantum defect value (δ) seems to be related to an *n*s Rydberg series. The $n = 5$ and $n = 6$ members might be responsible for a feature around 12.420 eV and a poorly resolved feature at 12.984 eV (Fig. 2). The quantum defect values (Table 1) seem to be slightly higher for a series of this type and this might be attributed to a mixed Rydberg-valence character for the transitions. The rather intense band centred at 11.431 eV (Fig. 2) corresponds to a state with a quantum defect value of 1.68 suggesting a 4p term (Table 1). The $n = 5$ and $n = 6$ terms are expected to have spectral bands at 12.74 and 13.23 eV. As the latter must be of lower intensity than the $n = 4$ band, they might be not distinguishable from the features around 12.90 and 13.4 eV (Fig. 2).

The 11.431 eV band might also be the first term of a nd series converging to the second ionisation limit with δ of 0.96. Then the second member is expected to be around 13.20 eV (on the low energy side of the 14.185 eV band (Fig. 2, Table 1). The other three series presented, converging to the 15.632, 16.461 and 16.845 eV ionisation limits respectively, have been assigned to *n*s series with $\delta \sim 2.00$ (Table 2). This is a tentative assignment as the $n = 4$ term of each series is of much lower intensity than the $n = 5$ member.

Hence, additional experiments and calculations are necessary to clarify the type of transitions involved in this energy region.

3.2. Cross section, photolysis rate and global warming potential (GWP)

The present measured cross section values over the energy range 4–11 eV, with a single local maximum value of 17.078 Mb at 9.336 eV and a value of 6.46 Mb at the Lyman alpha wavelength (121.6 nm), are considerably lower than the recent photo-absorption data reported by Chim et al. [14] who reported a cross section at 121.6 nm of 15 Mb. We have recorded a similar spectrum using the UK Daresbury synchrotron facility, in a different cell configuration and with a different gas sample and obtained cross sections within 5% of the present cross section values, thus, we estimate our values for the cross sections to be accurate.

The photolysis rates of SF_5CF_3 may then be evaluated as the product of the solar actinic flux [27] and molecular photo-absorption cross section at different altitudes and wavelengths. Using our cross sections we have evaluated the photolysis rates for SF_5CF_3 from ground level up to the stratopause (50 km) in 1 km steps. It is remarkable that there is no overlap between the solar flux and the photo-absorption spectrum at altitudes lower than 50 km, but actually an energy gap of about 1 eV, meaning that the SF_5CF_3 sink mechanisms at these altitudes must be by other than direct photolysis. In contrast at higher altitudes there is fairly good overlap, in particular at the Lyman alpha energy (10.2 eV). Due to the considerably smaller concentrations of UV absorbing species in the upper atmosphere there are considerably higher fluxes of higher energy photons available. Hence, it is likely that photo-dissociation of SF_5CF_3 will only occur in the ionosphere or mesosphere regions of the atmosphere. Indeed, the height profiles of SF_5CF_3 through the stratosphere obtained by Sturges et al. [1] support this conclusion. It is this long lifetimes at low altitudes that makes SF_5CF_3 such a strong greenhouse gas.

Recent studies of the reactions of SF_5CF_3 with positive ions in the stratosphere and/or ionosphere [7–9] have shown that ion–molecule reactions may remove this molecule from the Earth's atmosphere. But, electron attachment studies strongly suggest that dissociative electron attachment is one of the dominant processes in the lower ionosphere [10,11] and an atmospheric lifetime of around 1000 years seems reasonable. However, a more detailed investigation of the reactions of SF_5CF_3 on ice and dust surfaces, in particular the study of the reactivity of gaseous SF_5CF_3 with surfaces is required and is currently being performed [28] to understand how these mechanisms can affect the lifetime and reactivity of this gas in the terrestrial atmosphere.

Using recent IR absorption cross sections [5] we can now determine the radiative forcing of trifluoromethyl sulphur pentafluoride to be $(0.60 \pm 0.03)\,\mathrm{W\,m^{-2}\,ppb^{-1}}$, slightly greater (∼1.7–5%) than previously reported [1,7]. This value represents the largest radiative forcing on a per molecule basis of all gases present in the atmosphere. Assuming the atmospheric lifetime of the molecule to be 1000 years [6], we calculate the GWP of SF_5CF_3 over 100 years as 18,500, comparable with that of SF_6 (GWP ∼ 22,200 [29], atmospheric lifetime ∼ 3600 [30]). Therefore, it is important to identify current sources of atmospheric SF_5CF_3 in order to prevent further emissions.

4. Conclusions

A comprehensive analysis of the structure in the high resolution VUV photo-absorption cross section, in the range 5.5–11 eV ($225 > \lambda > 110$ nm), and EEL spectrum, in the range 7–23 eV, has been done. Rydberg series converging to the ionisation energies corresponding to the bands observed in the HeI photoelectron spectrum have been discussed for the first time. The lack of overlap between the photo-absorption spectrum of SF_5CF_3 and the solar flux at altitudes below 50 km means that photo-dissociation cannot occur in the troposphere or stratosphere. However, in the ionosphere/mesosphere, where the solar UV spectrum is stronger, photo-dissociation can take place. The lifetime of SF_5CF_3 in the Earth's atmosphere will be between several hundred and a few thousand years with the upper limit being the lifetime of the fluorinated un-substituted SF_6 molecule (3200 years).

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