CF3SF5 - a 'super' greenhouse gas

Tuckett, Richard

Document Version
Peer reviewed version

Citation for published version (Harvard):
Tuckett, R 2008, 'CF3SF5 - a 'super' greenhouse gas', *Education in Chemistry*, no. 45, pp. 17-21.

Link to publication on Research at Birmingham portal

CF_3SF_5 : a 'super' greenhouse gas

R. P. Tuckett

Education in Chemistry (2008) **45**, 17-21

Professor Richard Tuckett (University of Birmingham) / July 2011

CF₃SF₅ : another very potent greenhouse gas

Richard Tuckett

School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, U.K.

Abstract   One molecule of the anthropogenic pollutant trifluoromethyl sulphur pentafluoride (CF_3SF_5), an adduct of the CF_3 and SF_5 free radicals, causes more global warming than one molecule of any other greenhouse gas yet detected in the Earth's atmosphere. That is, it has the highest *per molecule* radiative forcing of any greenhouse pollutant, and the value of its global warming potential is only exceeded by that of SF_6. First, the greenhouse effect is described, the properties of a molecule that cause it to be a significant greenhouse gas, and therefore the contributions that physical chemistry can make to an improved understanding of the effect. Second, the chemistry of CF_3SF_5, first discovered in the atmosphere in 2000, is taken as a case study. Experiments using tunable vacuum-UV radiation, electrons and small cations have determined some of the relevant physical properties of this molecule, including the strength of the CF_3-SF_5 covalent bond. The main sink route to remove CF_3SF_5 from the earth's atmosphere is low-energy electron attachment in the mesosphere. Third, it is shown how such data are important inputs to determine the lifetime of this pollutant, *ca.* 1000 years, in the atmosphere. Finally, the generic lessons that can be learnt from the study of such long-lived greenhouse gases are described.

Introduction

An article in this journal seven years ago highlighted the environmental impact of sulphur hexafluoride, SF_6, on the earth's atmosphere, and in particular its contribution to global warming *via* the greenhouse effect.[1] In this article I describe some physical and chemical properties of a related molecule, trifluoromethyl sulphur pentafluoride *or* CF_3SF_5, first discovered to be an environmental problem at approximately the same time.[2] Over the last seven years, the importance of greenhouse gases and global warming has leapt from obscurity to the top of the polital agenda in all developed countries, culminating in the Stern report of November 2006 when the economic consequences of unchecked global warming were spelt out. It is therefore an appropriate time to review the science of the greenhouse effect (or more accurately radiation trapping) and describe what constitutes a 'serious' greenhouse gas, taking CF_3SF_5 as a case study. I review some of my research group's experiments on this molecule, and put CF_3SF_5 into the context of other greenhouse gases.[3] This article formed the basis of the opening seminar of the new Royal Society of Chemistry ChemNet initiative in December 2006.[4] The powerpoint file of this talk can be downloaded, with the usual health warning that the opinions expressed are my own, and others may disagree with them.

What constitutes a serious greenhouse gas?

The biggest myth in the general public's understanding of atmospheric science is that the greenhouse effect is all 'bad news'. Nothing could be further from the truth. Indeed, without the greenhouse effect the *average* temperature of our planet would be very cold, 256 K or $-17\ ^{o}C$. It is the greenhouse effect, *via* absorption and trapping of infrared radiation emitted by the earth and absorbed in the atmosphere by small polyatomic molecules such as CO_2, CH_4 and H_2O, that has raised the average temperature to a hospitable ~290 K. This is often called the 'natural' greenhouse effect, and has meant that the earth's temperature has remained approximately static for hundreds of years up to the start of the Industrial Revolution, *ca.* 1750. When the general public mention the greenhouse effect, they are really describing the 'enhancing' effect, caused by *increases* in concentration of greenhouse gases over the last 250 years. Nobody really doubts the scientific evidence that the concentration of the principal greenhouse gas, CO_2, has increased by *ca.* 35% over this time period from ~280 to ~380 parts per million by volume (ppmv), whilst the average temperature has also increased by ~1 ^{o}C. What has not yet been proven is that there is a cause-and-effect correlation between these two facts. That said, as demonstrated by the IPCC reports of 2007,[5] the consensus of world scientists, and certainly physical scientists, is that the CO_2 concentration and the temperature of the planet are strongly correlated, but there remain a small vociferous minority who believe otherwise.

Although most attention has rightly been given to CO_2 (and possibly CH_4 and H_2O), physical scientists now understand that there are larger polyatomic gases of low concentrations in the atmosphere which can

3

contribute significantly to global warming, as they absorb infrared radiation strongly in regions where CO_2, CH_4 and H_2O do *not* absorb. Two examples are SF_6 and CF_3SF_5. In qualitative terms, there are two properties that are necessary for a molecule to be an effective greenhouse gas. First, it must absorb IR radiation strongly in the black-body range of the Earth's emission, *ca.* 5–25 μm, where CO_2 *etc.* do not absorb ; in practice, many C–F and C–Cl stretching vibrations around 10 μm contribute strongly. Such transitions are only observed if the vibration causes a change in dipole moment of the molecule. Note that the vibrations of N_2 and O_2, comprising 99% of the earth's atmosphere, are infrared inactive. Second, the molecule must have a long lifetime in the atmosphere ; it must not be destroyed by photodissociation in the range 200–600 nm, and it must not react with the free radicals prevalent in the atmosphere. Furthermore, a greenhouse gas whose concentration is increasing rapidly due to mankind's activity will cause special concern. The new greenhouse gas CF_3SF_5 satisfies these criteria, and Table I shows data for four greenhouse gases : CO_2 and CH_4 which together cause ~70% of the total radiation trapping, a chlorofluorocarbon CF_2Cl_2, and CF_3SF_5.

The radiative forcing measures the strength of the IR absorption bands over the range 5–25 μm, it is a *per molecule* microscopic property with units of W m^{-2} per unit concentration. When multiplied by the change in concentration of pollutant over a defined time window, usually 250 years from the start of the Industrial Revolution to the current day, the *macroscopic* radiative forcing in units of W m^{-2} is obtained. One may then compare the effect of different pollutant molecules over this time window. The greenhouse potential (GHP), sometimes called the global warming potential, measures the radiative forcing, A_x, of a pulse emission of a greenhouse gas, x, over a defined time period, t, usually 100 years, relative to the time-integrated radiative forcing of a pulse emission of an equal mass of CO_2 :

$$\text{GHP}_x(t) \;=\; \frac{\int_0^t A_x(t).dt}{\int_0^t A_{CO2}(t).dt} \tag{I}$$

The GHP is therefore a dimensionless number that informs how important one unit of mass (*e.g.* 1 kg) of pollutant x is to the greenhouse effect *via* global warming compared to the same unit of mass of CO_2. The GHP of CO_2 is defined to be unity. With certain approximations,[3] equ. (I) can be simplified to give an analytical expression for the GHP of x over a time period t :

$$\frac{GHP_x(t)}{GHP_{CO2}(t)} \;=\; \frac{MW_{CO2}}{MW_x} . \frac{a_{o,x}}{a_{o,CO2}} . \frac{\tau_x}{K_{CO2}} . \left[1 - \exp\left(\frac{-t}{\tau_x} \right) \right] \tag{II}$$

The GHP of x therefore only incorporates values for the microscopic radiative forcing, a_o, of greenhouse gases x and CO_2 ; the molecular weights of x and CO_2 ; the lifetime of x in the atmosphere, τ_x ; and the constant K_{CO2} which can be determined for any value of t.[3] K_{CO2} has units of time, and is related (but not equal) to the lifetime of CO_2 in the atmosphere, whose values range from 50 to 200 years.[3] The macroscopic overall contribution of a pollutant to the greenhouse effect involves a complicated convolution of its concentration, lifetime and GHP value. Thus CO_2 and CH_4 contribute most to the greenhouse effect simply due to their high atmospheric concentration ; note that the microscopic radiative forcing and GHP of both gases are relatively low. Indeed, the vibrational mode of CO_2 at 15.0 μm, which is most responsible for greenhouse activity in CO_2, is close to saturation. By contrast, CF_3SF_5 has the highest microscopic radiative forcing of any known greenhouse gas (earning it the title 'super' greenhouse gas), even higher than that of SF_6. The GHP of these two molecules is therefore very high, SF_6 being slightly higher because its atmospheric lifetime, 3200 years,[3] is about three times greater than that of CF_3SF_5. However, the contribution of these two molecules to the overall greenhouse effect is still relatively small because their atmospheric concentrations, despite rising rapidly, are still very low, at the level of parts per trillion by volume.

CF_3SF_5 : its atmospheric properties

CF_3SF_5 is a gas at room temperature with a boiling point of 253 K and an enthalpy of vapourisation of 20 kJ mol^{-1}. Sturges et $al.$[1] first reported detection of CF_3SF_5 in the earth's atmosphere in 2000. Its source was believed to be anthropogenic, and most likely a breakdown product of SF_6 in high-voltage equipment. Since the trends in concentration levels of SF_6 and SF_5CF_3 have tracked each other very closely over the last 30-40 years (Fig. 1), Sturges et $al.$ suggested that CF_3SF_5 has mainly been produced in the electronics industry via the recombination of CF_3 and SF_5 free radicals. Absolute IR absorption measurements have shown that CF_3SF_5 has the highest microscopic radiative forcing of any gas found in the atmosphere to date, 0.60 ± 0.03 W m^{-2} ppbv^{-1}. Measurements taken from ice samples in Antarctica suggested that it has grown from a concentration of near zero in the late 1960s to $ca.$ 0.12 pptv in 1999 (or $ca.$ 2.5 x 10^6 molecules cm^{-3}) with a current growth rate of $ca.$ 6% per annum, and stratospheric profiles suggested that the lifetime of this species in the atmosphere is between several hundred and a few thousand years. In historical terms, the story of the chlorofluorocarbons, and their evolution over a period of less than twenty years from industrially-produced benign molecules to serious ozone-depleting molecules in the stratosphere, haunts the memory of many atmospheric scientists. Small problems in this area of science have a tendancy to become big problems. Thus, although the best estimate two years ago was that CF_3SF_5 only contributes 0.003 % to the total radiation trapping,[3] it is not surprising that there has been huge interest in its reactive and photochemical properties.

The reactions that remove CF$_3$SF$_5$ from the atmosphere are important as they contribute to its lifetime and GHP value. The total removal rate per unit volume per unit time is :

$$\text{Rate} \; = \; [\text{SF}_5\text{CF}_3].\left(k_1[OH] \; + \; k_2[O^*] \; + \; \sum_{ions} k_{ion}[ion] \; + \; k_e[e^-] \; + \; \sum_{\lambda} \sigma_{\lambda} J_{\lambda} \Phi_{\lambda} \right) \qquad \text{(III)}$$

where each of the five terms in the large bracket of equ. (III) is a pseudo-first-order rate constant. $[x]$ represents the concentration of species x. The first four terms represent reactions of CF$_3$SF$_5$ with OH, O*, cations and electrons, respectively ; k_i are the corresponding second-order bimolecular rate coefficients. OH radicals and electronically-excited O atoms, O*, are the most important oxidising free radicals in the atmosphere. The first term dominates in the troposphere ($0 <$ altitude (h) < 10 km), the second term in the stratosphere ($10 < h < 50$ km), and the third and fourth terms in the mesosphere ($h > 50$ km). In the fifth term, σ_{λ} and J_{λ} are the absorption cross section for CF$_3$SF$_5$ and the solar flux, respectively, and Φ_{λ} is the quantum yield for dissociation at wavelength λ. In the troposphere, the summation for λ is over the range *ca.* 290-700 nm, in the stratosphere *ca.* 200-290 nm, and in the mesosphere the solar flux at the Lyman-α wavelength of 121.6 nm dominates all other VUV wavelengths. Equ (III) assumes that the ion-molecule and electron attachment reactions lead to the removal of CF$_3$SF$_5$ by formation of dissociation products. Furthermore, secondary reactions of such products must not recycle CF$_3$SF$_5$.

Our first contribution was to measure, albeit in an indirect manner, the strength of the CF$_3$–SF$_5$ bond that connects the two radicals.[6] We used tunable VUV radiation from the UK Daresbury synchrotron source to photoionise CF$_3$SF$_5$. We measured the translational kinetic energy release as CF$_3$SF$_5^+$ dissociated into CF$_3^+$ + SF$_5$ as a function of photon energy, and obtained the first dissociative ionisation energy of this molecule (*i.e.* $\Delta_r H^o$ at 0 K for the reaction CF$_3$SF$_5$ $\rightarrow$ CF$_3^+$ + SF$_5$ + e$^-$). We found that the CF$_3$–SF$_5$ bond has strong σ-character with a dissociation energy as high as 372 ± 43 kJ mol^{-1}, a slightly surprising result. It confirmed, however, that UV photolysis in the stratosphere was very unlikely to contribute to the rate of removal of CF$_3$SF$_5$ from the atmosphere. We have since made laboratory-based measurments relevant to the mesosphere, where ionic processes involving cations, anions, electrons and VUV photoexcitation at 121.6 nm dominate. We measured rate coefficients and product yields of small cations reacting with CF$_3$SF$_5$ in a flow tube, the rate coefficient of low-energy electrons reacting with CF$_3$SF$_5$, and the absorption cross section of CF$_3$SF$_5$ at 121.6 nm.[3] The dominant process removing CF$_3$SF$_5$ from the mesosphere is low-energy electron attachment (*ca.* 99%), with VUV photodissociation only making a minor contribution (*ca.* 1%). Ion-molecule reactions make negligible contribution, not because the rate coefficients are too low but because the concentration of the relevant ions in the mesosphere (*e.g.* N$^+$, N$_2^+$) in equ (III) are too small.

The lifetime of CF$_3$SF$_5$ in the earth's atmosphere.

The lifetime of a greenhouse gas can be a confusing term. To a physical chemist, it means the inverse of the pseudo-first-order rate constant of the dominant chemical or photolytic process that removes the pollutant from the atmosphere. Using CH$_4$ as an example, it is removed in the troposphere *via* oxidation by the OH free radical, OH + CH$_4$ → H$_2$O + CH$_3$. The rate coefficient for this reaction at 298 *K* is 6.4 x 10^{-15} cm^3 molecule^{-1} s^{-1}, so the lifetime is approximately equal to $(k_{298}[OH])^{-1}$. Assuming the tropospheric OH concentration to be 0.1 pptv or 10^6 molecules cm^{-3}, the lifetime of CH$_4$ is calculated to be *ca.* 5 years. This is within a factor of 2.4 of the accepted value of 12 years (Table I). The difference arises because CH$_4$ is not emitted uniformly from the earth's surface, a finite time is needed to transport CH$_4$ *via* convection and diffusion into the troposphere, and oxidation occurs at different altitudes in the troposphere where the OH concentration varies from its average value of 10^6 molecules cm^{-3}. We can regard this as an example of a two-step kinetic process, A → B → C, with first-order rate constants k_1 and k_2. The first step, A → B, represents the transport of the pollutant into the atmosphere, whilst the second step, B → C, represents the chemical or photolytic process (*e.g.* reaction with an OH radical in the troposphere, electron attachment in the mesosphere) that removes the pollutant from the atmosphere. In general, the overall rate of the process (whose inverse is called the *lifetime*) will be a function of both k_1 and k_2, but its value will be dominated by the *slower* of the two steps. Thus, in writing the lifetime of CH$_4$ simply as $(k_{298}[OH])^{-1}$, we are assuming that the first step, transport into the region of the atmosphere where chemical reactions occurs, is very fast with $k_1 \gg k_2$.

CF$_3$SF$_5$ behaves in the opposite sense, and now $k_1 \ll k_2$. The slow, rate-determining process is the first step, transport of the greenhouse gas from the surface of the earth into the mesosphere, and the chemical or photolytic processes that remove CF$_3$SF$_5$ in the mesosphere will have very little influence on the lifetime. We can define a chemical lifetime, $\tau_{chemical}$, as $(k_e[e^-] + \sigma_{121.6}J_{121.6}\Phi_{121.6})^{-1}$, but its value will vary with altitude. In the troposphere, $\tau_{chemical}$ will be infinite because both the concentration of electrons and $J_{121.6}$ are effectively zero, but in the mesosphere $\tau_{chemical}$ will be much less. Assuming the electron attachment step is dominant, multiplication of k_e for CF$_3$SF$_5$ by a typical electron density in the mesosphere yields a chemical lifetime which is far too small and bears no relation to the true atmospheric lifetime, simply because most of the CF$_3$SF$_5$ does not reside in the mesosphere. Using calibration data for SF$_6$, the globally-averaged lifetime of ~1000 years for CF$_3$SF$_5$ (Table I) comes from a weighted integration of the removal rates in the different regions of the atmosphere. Its lifetime is therefore determined by the meterology that transports it into the mesosphere, and the chemical fate of each molecule when it reacts in that region with low-energy electrons and Lyman-α radiation only makes negligible contribution to the atmospheric lifetime.

General comments on long-lived greenhouse gases.

In 1994, six years before this CF_3SF_5 story began, Ravishankara *et al.*[7] wrote that the release of any long-lived species into the atmosphere should be viewed with great concern. They noted that chlorofluorocarbons, with relatively 'short' lifetimes of ~100 years, have had a disastrous effect on the stratosphere, but following implementation of international treaties (*e.g.* Montreal, 1987) the ozone layer should recover within 50–100 years. At present, there are no known undesired chemical effects of low concentrations of CF_3SF_5 (and SF_6) in the atmosphere. However, their rapidly-increasing concentrations and their *exceptionally* long lifetimes means that life on earth may not be able to adapt to any changes these gases may cause in the future. They suggested that all such long-lived molecules should be considered guilty, unless proven otherwise. One solution is to discover inert, dielectric gases with low GHP values which could be used as substitutes for SF_6 in industrial applications. Ring-based perfluorocarbons, such as *cyclic*-C_4F_8 and *cyclic*-C_5F_8 are possibilities. However, the simplest, possibly naïve, suggestion is that we should not put up into the atmosphere any more pollutants than are absolutely necessary. The worldwide debate just starting is what constitutes 'absolutely necessary'.

References

1. G. Rayner-Canham and A. Hewlin, *Educ. in Chem.,* 2000, **37**, 69.
2. W.T. Sturges, T.J. Wallington, M.D. Hurley, K.P. Shine, K. Sihra, A. Engel, D.E. Oram, S.A. Penkett, R. Mulvaney, C.A.M. Brenninkmeijer, *Science*, 2000, **289**, 611.
3. R.P. Tuckett, *Adv. in Fluorine Science*, 2006, **1**, chapter 3, pp.91–131 (Elsevier).
4. http://www.rsc.org/Membership/Networking/ChemNet/pastevents.asp
5. http://www.ipcc.ch
6. R.Y.L. Chim, R.A. Kennedy, R.P. Tuckett, W. Zhou, G.K. Jarvis, D.J. Collins and P.A. Hatherly, *J. Phys. Chem. A.,* 2001, **105**, 8403
7. A.R. Ravishankara and E.R. Lovejoy, *J. Chem. Soc. Faraday Trans.,* 1994, **90**, 2159.
8. R.A. Kennedy and C.A. Mayhew, *Int. J. Mass Spectrom.,* 2001, **206**, i.

Figure Captions

Figure 1   Structure and sources of CF_3SF_5. The graphs show how the concentrations of CF_3SF_5 and SF_6 in the earth's atmosphere have tracked each other very closely since 1970, and how air extracted from Antarctic ice samples show very similar variations of concentration of the two chemicals with depth below the earth's surface (with permission from Sturges *et al.*[2])

Figure 2   Calculated IR absorption spectrum of CF_3SF_5 using Gaussian 03. The molecule has 24 vibrational modes, but only 6 have any significant IR intensity. The four most intense bands occur in the atmospheric window, where CO_2, CH_4 and H_2O do not absorb, of 8–14 μm or 730–1260 cm^{-1} (with thanks to Michael Parkes, PhD thesis, University of Birmingham, 2007)

Figure 3   Apparatus used to determine the first dissociative ionisation energy of CF_3SF_5, by measuring correlated appearance of threshold photoelectrons and mass-selected photoions as a function of vacuum-UV wavelength. The apparatus can also study the correlated appearance of threshold photoelectrons or mass-resolved cations with fluorescence photons, but these modes of operation are not used in this work.

Figure 4   (a) Mean total kinetic energy released in the reaction $CF_3SF_5 + h\nu \rightarrow CF_3^+ + SF_5 + e^-$ for photon energies in the range 13.3 to 15.5 eV. The error in each value of the kinetic energy is *ca.* 20 %. A linear extrapolation to zero kinetic energy gives the first dissociative ionisation energy of CF_3SF_5 to be 12.9 ± 0.4 eV. We then determine the strength of the CF_3–SF_5 bond to be 3.86 ± 0.45 eV or 372 ± 43 kJ mol^{-1}, and the enthalpy of fomation of CF_3SF_5 at 0 *K* to be -1750 ± 47 kJ mol^{-1}. (b) Threshold photoelectron spectrum of SF_5CF_3 over the same range of energies (with permission from Chim *et al.*[6])

Figure 5   Electron attachment results for CF_3SF_5. Rate coefficient as a function of mean electron energy, ε, in atmospheric pressure of N_2 ($\varepsilon < 0.5$ eV) and Ar ($\varepsilon > 0.5$ eV). The thermal rate coefficient at 298 *K*, where $\varepsilon = 0.038$ eV, is 7.7 ± 0.6 x 10^{-8} cm^3 $molecule^{-1}$ s^{-1}, and the sole product is dissociative, SF_5^- (with permission from Kennedy *et al.*[8])

Table I Examples of four greenhouse gases and their contribution to global warming

Greenhouse gas	CO_2	CH_4	CF_2Cl_2	CF_3SF_5
Concentration / ppmv	380	1.75	0.0005	1.2×10^{-7}
$\Delta Conc^n$ (1750−2000) / ppmv	100	1.05	0.0005	1.2×10^{-7}
$\Delta Conc^n$ currently / % per year	0.45	0.60	*ca.* 5.0	*ca.* 6.3
Microscopic radiative forcing / W m^{-2} ppbv^{-1}	1.68×10^{-5}	4.59×10^{-4}	0.32	0.60
Total radiative forcing [a] / W m^{-2}	1.46	0.48	0.16	7.2×10^{-5}
Lifetime [b] / years	50−200 [c]	12	100	~1000
GHP (100 year projection)	1	23	10600	~18000
Contrib^n to GH effect / %	52	17	~6 [d]	0.003

[a] Due to change in concentration of greenhouse gas from the pre-Industrial era to the present time.

[b] Assumes a single-exponential decay for removal of greenhouse gas from the atmosphere.[3]

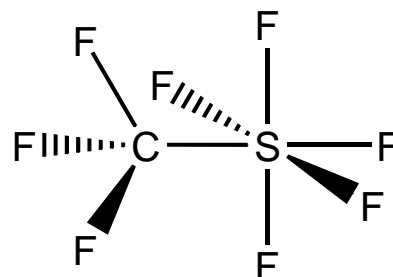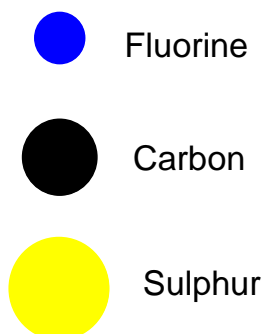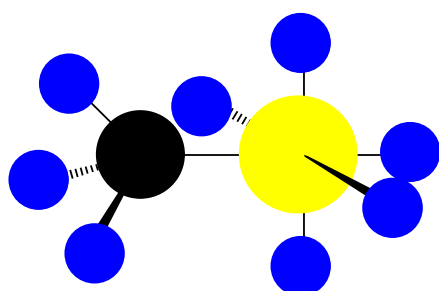[c] CO_2 does not show a single-exponential decay.[3]

[d] Cumulated effect of all chlorofluorocarbons is estimated to be 15%.

Table II   Thermal electron attachment rate coefficients, absorption cross-sections at 121.6 nm, and atmospheric lifetimes for CF_4, SF_6 and CF_3SF_5. From these data CF_3SF_5 appears to behave as a perturbed SF_6, and not as a perturbed CF_4 molecule.

Perfluoro compound	k_e (298 K) / cm^3 s^{-1}	$\sigma_{121.6}$ / cm^2	lifetime / years
CF_4	$< 10^{-16}$	$< 8 \times 10^{-22}$	> 50000
SF_5CF_3	7.7×10^{-8}	1.3×10^{-17}	~ 1000
SF_6	2.38×10^{-7}	1.76×10^{-18}	~ 3200

Figure 1

Structure of CF$_3$–SF$_5$

Fluorine

Carbon

Sulphur

Sources of CF$_3$–SF$_5$

- **Anthropogenic.**

- **SF$_6$ a dielectric in high-voltage applications.**

- **By-product of SF$_5$· reacting with CF$_3$· (from fluoropolymers)**
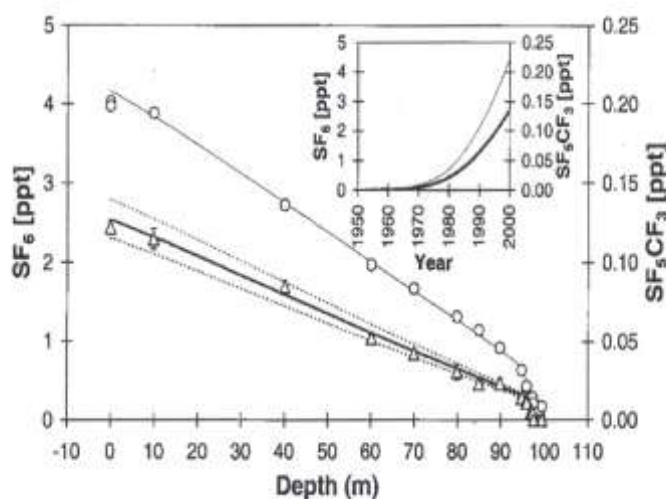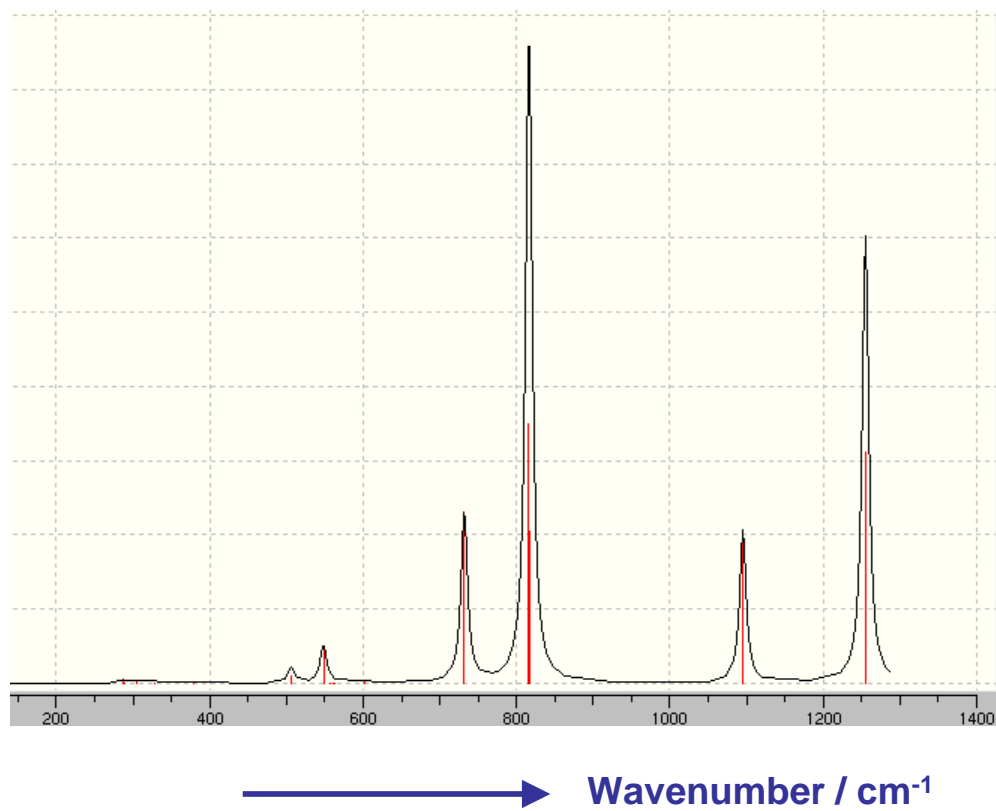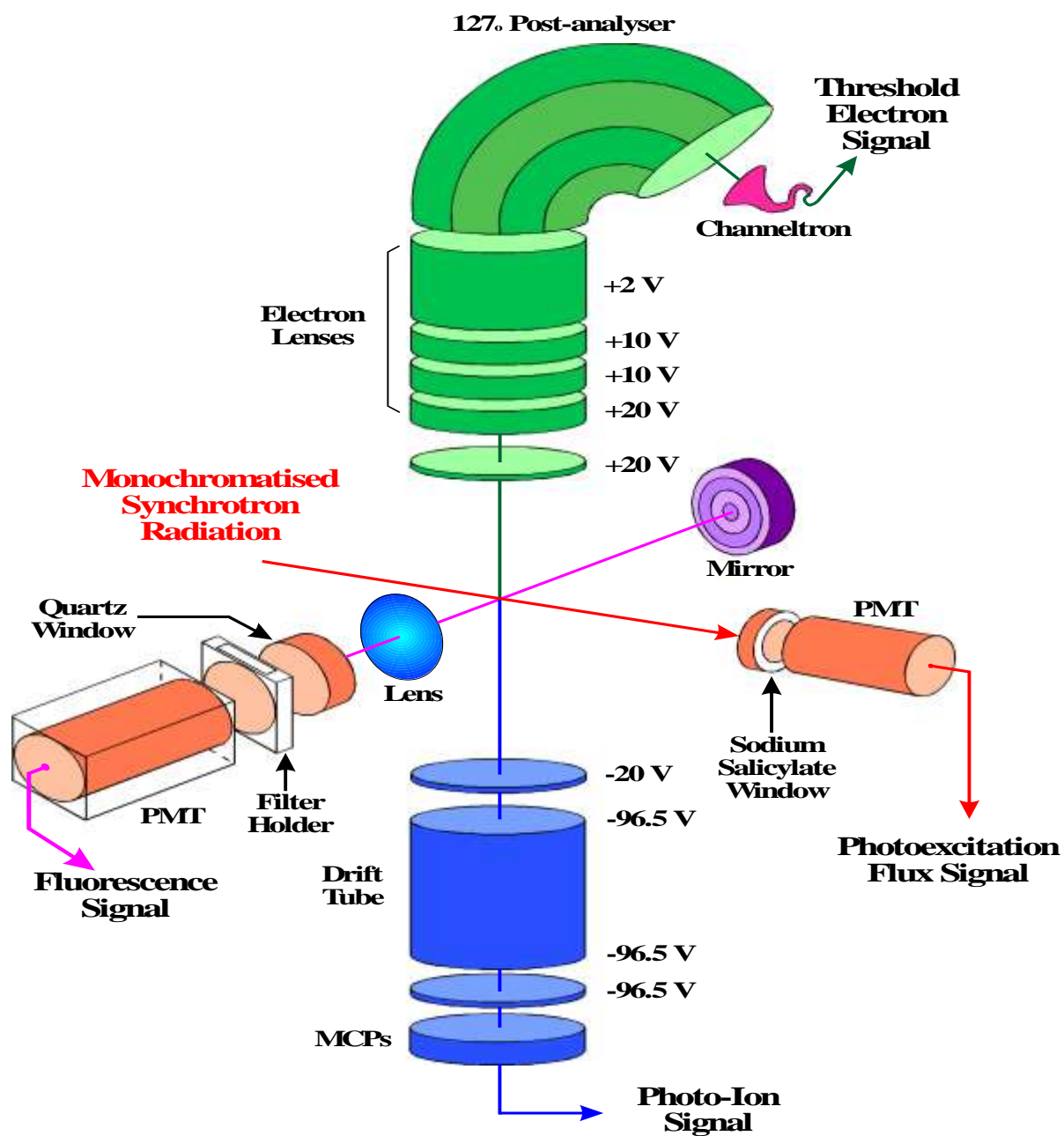
Figure 2

Wavenumber / cm⁻¹

Figure 3

Figure 4

Figure 5