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SF_5CF_3 : the atmospheric properties of this ultimate greenhouse gas
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Abstract: One molecule of SF_5CF_3, an adduct of the $SF_5\cdot$ and $CF_3\cdot$ free radicals, causes more global warming than one molecule of any other greenhouse gas. Using coincidence spectroscopy at the Daresbury SRS, we have determined the strength of the S−C bond to be as large as 3.86 ± 0.45 eV or 372 ± 43 kJ mol^{-1}. This molecule is therefore very unlikely to be removed from the earth's atmosphere by UV photolysis in the stratosphere. Complementary experiments at Birmingham and Super-Aco, Paris have shown that the main sink route of this greenhouse pollutant is low-energy electron attachment in the mesosphere, with Lyman-α photodissociation at 121.6 nm only being a minor channel. By comparison with data for SF_6, the lifetime of SF_5CF_3 in the earth's atmosphere is estimated to be ca. 1000 years.

Text: Serendipity, or being in the right place at the right time, has a long history in science. The accidental discovery of C_{60} by Harry Kroto et al. in 1985 is perhaps the most famous recent example. In early 2000, by chance I acquired an early preprint of a paper to appear later in the year (Sturges et al., *Science*, (2000) **289**, 611-613). It described the infrared absorption spectrum of a potent greenhouse gas, SF_5CF_3, and its detection in the earth's atmosphere. This molecule is an adduct of the $SF_5\cdot$ and $CF_3\cdot$ free radicals, and its origin is anthropogenic, i.e. man-made. Almost certainly, its source is the reaction of $SF_5\cdot$, a breakdown product of the dielectric SF_6 in high voltage equipment, with $CF_3\cdot$ on the surface of fluoropolymers ; when the Nuclear Structure Facility was in operation at Daresbury, the local concentration of SF_5CF_3 was probably enormous! Firn measurements made in Antarctica of air samples pumped out of consolidated snow suggested that the concentration of SF_5CF_3 at the end of the 20th century was still very small, ca. 0.12 parts per trillion or 3×10^{11} molecules cm^{-3}, but it was growing at the huge rate of 6 % per annum. As important, the strength of the infrared bands suggested that SF_5CF_3 has the strongest radiative forcing, on a per molecule basis, of any pollutant found in the earth's atmosphere. Small problems can become big problems in atmospheric chemistry, and this paper caused an explosion of interest world-wide to study the properties of this unusual molecule, especially those that pertain to its role in the earth's atmosphere. Chemists were particularly interested in the possible sink routes of this molecule from the atmosphere. Could UV photolysis in the stratosphere (15-50 km), the principle cause of ozone depletion by chlorofluorocarbons, remove SF_5CF_3 ? Or was the S−C σ bond strong enough that it survived processes occurring in the stratosphere, and it was removed at greater altitudes by processes in the mesosphere ?

Within months of receiving this preprint, using tunable vacuum-UV radiation in the range 12-25 eV from beamline 3.1 (Seya) of the SRS, we measured the threshold photoelectron – photoion coincidence (TPEPICO) spectrum of SF_5CF_3, and determined indirectly the strength of the S−C bond in the neutral molecule. The apparatus (Fig. 1) incorporates a threshold electron analyser, a linear time-of-flight mass spectrometer, a sodium salicylate window for flux normalisation, and software that allow TPEPICO spectra to be recorded continuously as a function of photon energy. Like CF_4^+ and SF_6^+, the ground state of $SF_5CF_3^+$ is repulsive in the Franck-Condon region along the S−C coordinate. The onset of ionisation

can therefore only give an upper limit to the energy of the first dissociative ionisation pathway of SF_5CF_3, to $CF_3^+ + SF_5 + e^-$. We have therefore determined the kinetic energy released into the two molecular fragments over a range of photon energies in the Franck-Condon region ; the raw data for $CF_4 \rightarrow CF_3^+ + F + e^-$ is shown as a 3-d false colour map in Fig. 2. Using an impulsive model for photodissociation, the data for SF_5CF_3 has been analysed and extrapolated to zero kinetic energy. In this way, we determined experimentally the first dissociative ionisation energy for SF_5CF_3 to be 12.9 ± 0.4 eV. Subtracting the adiabatic ionisation energy of the $CF_3\cdot$ radical, 9.04 ± 0.04 eV, we obtained $D^o_0(SF_5-CF_3)$ of 3.86 ± 0.44 eV or 372 ± 42 kJ mol^{-1}. The atmospheric significance of this value is that the S$-$C bond is a strong σ bond, and it is highly unlikely that SF_5CF_3 will be broken down by UV photolysis (200-400 nm) in the earth's stratosphere. Subsequently, the electron energy loss spectrum of SF_5CF_3 was measured by Nigel Mason's group, showing that excited electronic states of this molecule, a precursor for photodissociation, do not exist below 8 eV.

We therefore studied the processes that could remove SF_5CF_3 in the mesosphere above *ca.* 60 km ; reactions with small cations, with electrons, and Lyman-α (121.6 nm) photodissociation. The total rate of removal of SF_5CF_3 is then given by

$$ \text{Rate} \ = \ [SF_5CF_3].\left(\sum_{ions} k_{ion}[ion] \ + \ k_e[e^-] \ + \ \sigma_{121.6}J_{121.6} \right) \ \text{molecules cm}^{-3}\,\text{s}^{-1} \quad (1) $$

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. In Birmingham, Chris Mayhew and I measured the rate constants for the reactions of a number of atmospheric cations (*e.g.* N_2^+, O^+) with SF_5CF_3 in a selected ion flow tube, and Richard Kennedy measured k_e in an electron swarm apparatus (7.7×10^{-8} cm^3 molecule^{-1} s^{-1}). At the Super-Aco synchrotron in Paris, I measured the vacuum-UV absorption spectrum between 8 and 20 eV, and determined $\sigma_{121.6}$ to be 1.3×10^{-17} cm^2. By comparison with analogous data for SF_6, we showed that the ion-molecule term in equ.(1) is insignificant since the ion concentrations in the mesosphere are too low, Lyman-α photodissociation contributes *ca.* 1 %, but the dominant loss mechanism of SF_5CF_3 is low-energy electron attachment to form the dissociative SF_5^- anion. The atmospheric lifetime, however, is determined by the slowest step in a multi-step kinetic scheme, which is the rate of transport of SF_5CF_3 from the earth's surface to the mesosphere. The lifetime is estimated to be enormous, *ca.* 1000 years. We are stuck with this potential environmental problem for the foreseeable future!

Chim RYL, Kennedy RA, Tuckett RP, Zhou W, Jarvis GK, Collins DJ and Hatherly PA,
Fragmentation of state-selected SF_5-CF_3^+ probed by threshold photoelectron – photoion coincidence spectroscopy : the bond dissociation energy of SF_5-CF_3, and its atmospheric implications.
J. Phys. Chem. A., (2001) **105**, 8403-8412

Chim RYL, Kennedy RA and Tuckett RP,
Absorption spectrum of SF_5CF_3 in the range 8-20 eV ; implications for its atmospheric lifetime.
Chem. Phys. Letts., (2003) **367**, 697-703

Kennedy RA and Mayhew CA
Low-energy electron attachment to SF_5CF_3 : atmospheric implications
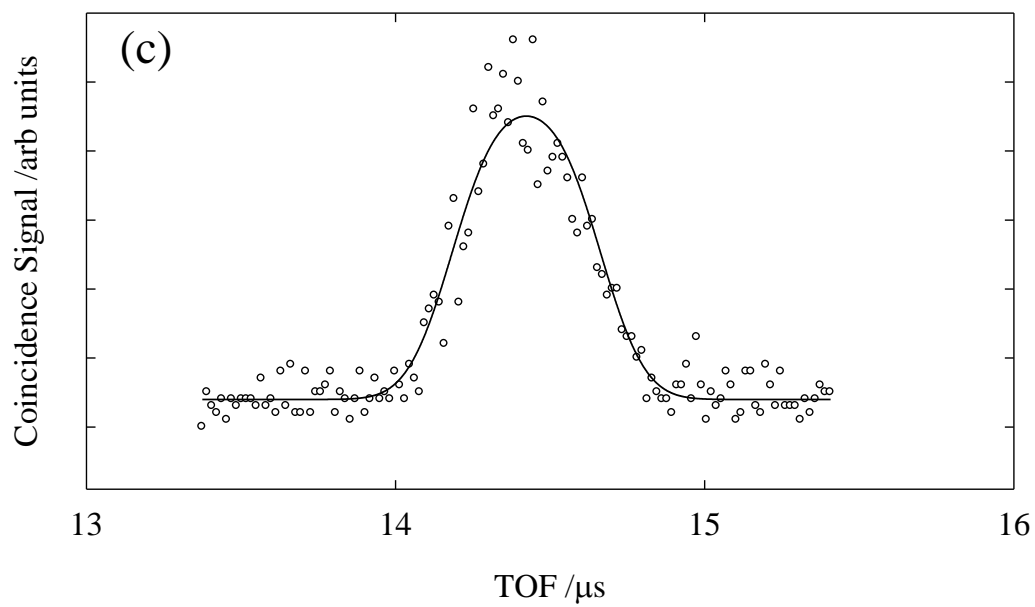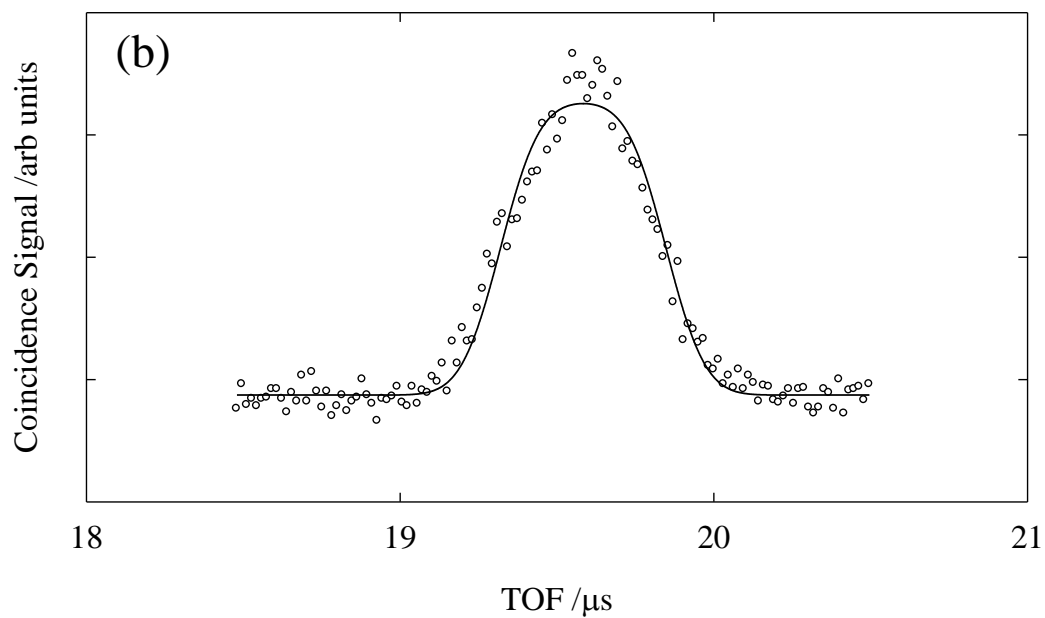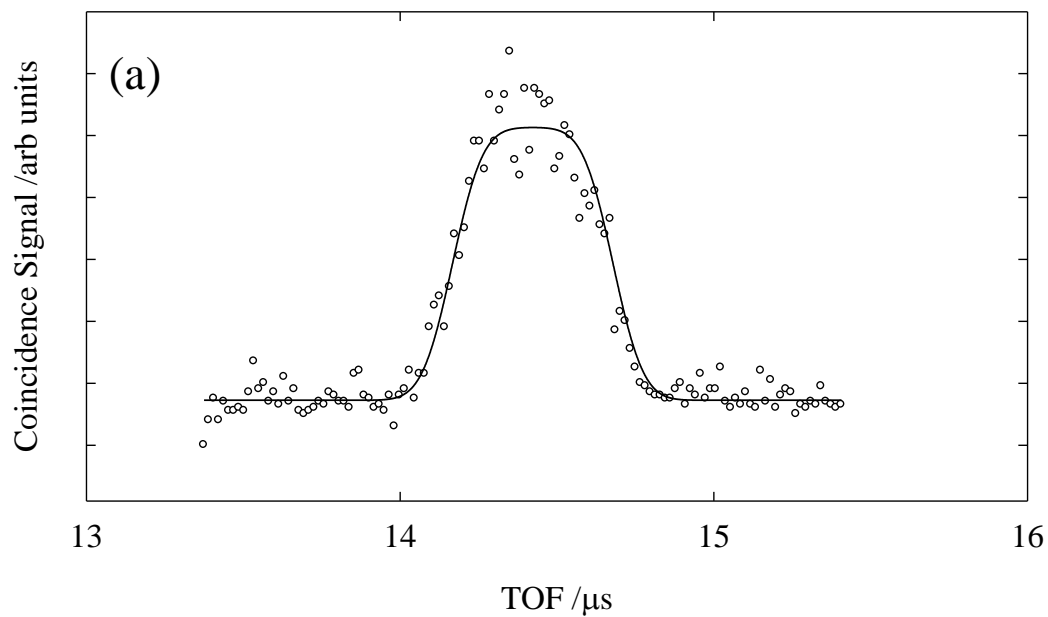*Int. J. Mass Spectrometry,* (2001) **206**, i-iv

Figure 1 Apparatus used to record threshold photoelectron - photoion coincidence (TPEPICO) spectra of $SF_5CF_3^+$. Monochromatised vacuum-UV photons in the range 12-25 eV from the Daresbury synchrotron is the tuneable photoionising source of radiation. The apparatus can also record coincidences between either threshold photoelectrons and fluorescence photons (TPEFCO) or photoions and fluorescence photons (PIFCO), but these modes are not used in this study.

Figure 2 TPEPICO-TOF spectra (open circles) for (a) CF_3^+ from CF_4, (b) SF_5^+ from SF_6, and (c) CF_3^+ from SF_5CF_3 recorded at photon energies of 16.05, 15.72 and 14.09 eV, respectively. Shown as solid lines, the data fit to mean kinetic energy releases of 0.81, 0.83 and 0.24 eV, respectively.

Figure 3 America is going to be hot in 2154! The images show the results of a computer climate model in which the atmospheric concentration of CO_2 increases at a compound rate of 1% per annum, *i.e.* the concentration doubles in 70 years. The CO_2 concentration then remains constant for 80 years as the climate adjusts to these higher levels. The image on the left shows the predicted temperature rise in the year 2154, that on the right is the 10-year average for the years 2145-2154. In both cases, the temperature changes are relative to a constant concentration of CO_2 at 2004 levels for the next 150 years. Note a big increase in predicted temperature over the populated North America continent, a smaller increase over the less-populated South America continent. The message is clear. We ignore global warming and the effects of pollutants, even minor ones such as SF_5CF_3, at our peril. Published by permission of Dr Jana Goldman (NOAA) from
http://www.gfdl.noaa.gov/products/vis/images/gallery/sphere_04_150.gif

Figure 1

Figure 2

Figure 3