Electron and photon induced processes in SF$_5$CF$_3$

P. Limão-Vieira$^{a,*}$, P.A. Kendall$^a$, S. Eden$^a$, N.J. Mason$^a$, J. Heinesch$^b$, M.-J. Hubin-Franskin$^b$, J. Delwiche$^b$, A. Giuliani$^b$

$^a$ Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK
$^b$ Laboratoire de Spectroscopie d’Electrons diffus, Université de Liège, Institut de Chimie-Bât. B6C, B-4000 Liège, Belgium

Abstract

The photo-absorption cross section of trifluoromethyl sulphur pentafluoride, SF$_5$CF$_3$, has been measured using synchrotron radiation in the range of 4–11 eV (310 nm > $\lambda$ > 110 nm) and comparison made with electron energy loss spectroscopy (EELS). The measured VUV cross sections are used to derive the photolysis rate of SF$_5$CF$_3$ in the terrestrial atmosphere. It is estimated that the lifetime for this molecule is the order of a 1000 years and the calculated global warming potential (GWP) is found to be between 17000 and 18100, making it one of the most potent global warming gases in the terrestrial atmosphere.

1. Introduction

Concern of the effect of climate change arising from global warming has grown over the last 20 years and is now the subject of major political discussions. The recent report of International Panel for Climate Change (IPPC) forecasts that mean global temperatures may rise by as much as 5.8°C by the end of the century (www.ipcc.ch, 2001). The major contributions to such global warming are strong greenhouse gases compounds such as CO$_2$, CH$_4$ and N$_2$O. However, there are number of gases which although present in much smaller quantities have a significant contribution to global warming due to their large infrared absorptions and long lifetimes in the terrestrial atmosphere.

A newly discovered totally anthropogenic origin molecule is trifluoromethyl sulphur pentafluoride (SF$_5$CF$_3$). According to a recent report (Sturges et al., 2000), it possesses the largest radiative forcing on a per molecule basis of all gases present in the atmosphere, 0.57 W m$^{-2}$ ppb$^{-1}$. Moreover, the levels in the atmosphere for this molecule although currently small, ~0.13 parts per trillion by volume, are growing at a 6% per year rate or in mass terms, the total burden is 3900 tonnes increasing at 210 tonnes per year.

Since SF$_5$CF$_3$ has no natural source its presence in the terrestrial atmosphere seems to be related to SF$_6$ radicals (a breakdown product of SF$_6$ formed by high-voltage discharges) in reaction with CF$_3$ radicals from fluoro-polymeric surfaces (Kennedy and Mayhew, 2001). SF$_6$ is used in high voltage circuit breakers due to its high dielectric strength, transformers, accelerators and other high voltage equipment.

The electron energy loss spectrum (EELS) of SF$_5$CF$_3$ has recently been measured and revealed that the threshold for the lowest-lying excited electronic state lies ~8 eV above the ground state (Kendall and Mason, 2001, 2003, respectively), confirming the prediction of a high dissociation energy for the SF$_5$–CF$_3$ bond (Gstir et al., 2002) of about 4 eV.

In this paper we report a high resolution, absolute photo-absorption spectrum of SF$_5$CF$_3$ in the energy range of 4–11 eV. The measured cross sections reveal a rich electronic structure and the predictions for the dissociation energy are confirmed.
range 5.5–11 eV (225 nm >λ > 110 nm) and discuss the implications for its lifetime in the terrestrial atmosphere.

2. Experimental apparatus

2.1. Photo-absorption

The photo-absorption spectrum presented in this paper was recorded on the ultraviolet vacuum line, UV1, of the Astrid synchrotron radiation facility (www.isa.au.dk) at the University of Aarhus, Denmark. The absorption cell and detection system used has been described elsewhere (Mason et al., 2003), so only a brief review is given here. The apparatus consisted of a simple 25 cm absorption path length static gas cell and a photomultiplier detector to record the transmitted light, \( I_t \) at 0.05 nm intervals with a typical resolution of 0.075 nm. As well as the transmitted light intensity, 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 sample cell is then evacuated and the radiation transmitted through the empty cell to record the background intensity, \( I_0 \). The absolute photo-absorption cross section is then evaluated by using the Beer–Lambert law:

\[
I_t = I_0 \exp(-\sigma n x),
\]

where \( n \) is the target gas number density, \( \sigma \) is the absorption cross section, and \( x \) is the path length (Mason et al., 1996). The minimum wavelength for which data could be collected is determined by the choice of entrance and exit windows in the gas cell, and for the present configuration, a LiF entrance window and a CaF\(_2\) exit window in front of the photomultiplier tube are used. Therefore, the lowest wavelength at which reliable data could be collected is 115 nm. To avoid any saturation effects (Gingell et al., 1999), the cross sections were measured over the pressure ranges 0.075–0.750 Torr, with typical attenuation of less than 10%. Precautions were also taken in order to avoid any second-order light effects.

2.2. Electron energy loss spectroscopy (EELS)

The EEL spectrometer used at University College London has been described in detail elsewhere (Davies et al., 1995). Briefly, thermionically emitted electrons are focused through a hemispherical energy selector and this selects the energy of the electron beam with a resolution of ~50 meV. A set of electron lenses in the electron spectrometer is used for imaging and energy control of the electron beam. The beam intercepts an effusive molecular beam at right angles, and scattered electrons are energy analysed into a second hemispherical analyser, with an acceptance angle of ~1°. The electrons pass through the analyser, which selects the energy loss to be detected, before entering the channeltron detector. The analyser can rotate about the interaction region to allow detection of electrons scattered at different angles. In this experiment, the angle was kept at ~0°.

\( \text{SF}_2\text{CF}_3 \) gas was purchased from Argo International Ltd. with a stated purity of 99.9% (although we detected a 0.04% CS\(_2\) contamination).

3. Results and discussion

The high-resolution photo-absorption cross section obtained (Fig. 1) shows no structure below 8 eV with the first absorption band reaching a local maximum cross section of 17.078 Mb at 9.336 eV. The value of the cross section at the Lyman-\( \alpha \) wavelength, 121.6 nm (10.197 eV), has recently been reported as being 15 Mb (Chim et al., 2002) considerably higher than the 6.459 Mb from our data. The feature close to 11 eV is only partially recorded due to the cut-off in the transmission of the CaF\(_2\) window.

The feature observed at 9.336 eV with no associated vibrational structure seems to be a transition to a valence state of the neutral molecule and is not a transition to a Rydberg state of the lowest ionisation energy 14.1 eV. Such a conclusion is confirmed by measurement of photoelectron spectra recorded at the University of Liège.

The EELS spectrum obtained for \( \text{SF}_2\text{CF}_3 \) is shown in Fig. 2 and a comparison is made with the VUV photo-absorption spectrum recorded at the synchrotron radiation facility, Denmark. The pseudo-absorption spectrum has been measured at near optical conditions (scattering angle ~0°) with electron impact energy of 150 eV, and its differential oscillator strength scaled to the absolute cross section values from the VUV photo-absorption experiment. The shapes of the two curves in this energy region are in good agreement and confirm that threshold for the first low lying electronic excitation lies at ~8 eV.

4. Photolysis rates

Since the first electronic excitation on \( \text{SF}_2\text{CF}_3 \) appears at ~8 eV solar photons are not able to photo-dissociate this molecule until the upper part of the stratosphere since the terrestrial ozone layer filters all UV radiation with energies <7 eV. The photolysis rates of \( \text{SF}_2\text{CF}_3 \) may be evaluated as the product of the solar actinic flux (NASA, 1997) and molecular photo-absorption cross section at different altitudes and wavelengths. The total rates shown in Fig. 3 are the summation over the wavelength range of these partial rates assuming...
that the quantum yield for photo-dissociation is assumed to be unity. The local lifetime to photolysis at a given altitude, also shown in Fig. 3, is thence the reciprocal of the total photolysis rate. The lifetimes are for a molecule with a fixed altitude in a sunlit, clear sky atmosphere.

While there is a fairly substantial photolysis rate at higher altitudes, above 30 km, leading to lifetimes of the order of a year, at lower altitudes the lack of solar actinic flux at the absorption wavelengths of this molecule leads to extremely long lifetime. It is this long lifetime at low altitudes coupled with its strong infrared

Fig. 1. The high-resolution total photo-absorption spectrum of SF₃CF₃ recorded at the ASTRID Synchrotron ring facility.

Fig. 2. Photo-absorption cross sections derived from EELS measurements (electron impact energy, 150 eV, scattering angle, 0°) compared to those collected using the ASTRID synchrotron facility.
absorption properties that make SF$_5$CF$_3$ such a strong greenhouse gas.

The 100 years global warming potential for this molecule assuming a lifetime of a 1000 years has been calculated to be between 17,500 and 18,600. The annual growth of this potentially powerful contributor to the anthropogenic greenhouse effect, SF$_5$CF$_3$, starts is therefore of concern. In fact if uncontrolled levels could reach high accumulation quantities, they could be sufficient to cause serious levels of global warming. Indeed even, if the emissions sourced were halted completely immediately, it will take around 1000 years to clean the atmosphere from this molecule.

5. Conclusions

The experimental results presented in this paper provide the high-resolution VUV photo-absorption spectrum of SF$_5$CF$_3$ in the range 4.0–11 eV (310–110 nm). Photolysis rates and local lifetimes of the molecule are calculated for various altitudes in the Earth’s atmosphere.
atmosphere and their impact on global warming discussed.

Acknowledgements

PLV acknowledges the Portuguese “Fundação para a Ciência e a Tecnologia” for a Postgraduate Scholarship; SE and NJM acknowledge the support of UK funding councils EPSRC, NERC and CLRC during the course of this research.

References