23. M. R. Drury and J. D. F. Fitz Gerald, *Geophys. Res. Lett.* **23**, 701 (1996); R. Wirth, *Contrib. Mineral. Petrol.* **124**, 44 (1996).
24. M. R. Carroll, D. S. Draper, R. A. Brooker, S. Kelley, in *Noble Gas Geochemistry and Cosmochemistry*, J. Matsuda, Ed. (Terra Scientific, Tokyo, 1994), pp. 325–341.
25. T. Matsumoto, M. Honda, I. McDougall, S. Y. O'Reilly, *Geochim. Cosmochim. Acta* **62**, 2521 (1998).
26. T. J. Dunai and H. Baur, *Geochim. Cosmochim. Acta* **59**, 2767 (1995).
27. G. L. Davies, *Carnegie Inst. Wash. Yearb.* **76**, 631 (1977).
28. C. R. Neal et al., in *Large Igneous Provinces: Continental, Oceanic, and Planetary Flood Volcanism* (*Geophys. Monogr. 100*, American Geophysical Union, Washington, DC, 1997), pp. 183–216.
29. A. D. Beard et al., *Lithos* **39**, 93 (1996).
30. We thank G. Pearson (Durham University, UK) for kindly providing the samples from Malaita and H. Downes (Birkbeck College, University of London) and P. Kempton (UK National Environment Research Council Isotope Unit) for providing the sample from Elovy Island. S.P.K. and J-A.W. greatly appreciate a grant from the Leverhulme Trust that allowed this work to be undertaken.

21 April 2000; accepted 12 June 2000

A Potent Greenhouse Gas Identified in the Atmosphere: SF₅CF₃

W. T. Sturges,[1] T. J. Wallington,[2] M. D. Hurley,[2] K. P. Shine,[3] K. Sihra,[3] A. Engel,[4] D. E. Oram,[1] S. A. Penkett,[1] R. Mulvaney,[5] C. A. M. Brenninkmeijer[6]

We detected a compound previously unreported in the atmosphere, trifluoromethyl sulfur pentafluoride (SF_5CF_3). Measurements of its infrared absorption cross section show SF_5CF_3 to have a radiative forcing of 0.57 watt per square meter per parts per billion. This is the largest radiative forcing, on a per molecule basis, of any gas found in the atmosphere to date. Antarctic firn measurements show it to have grown from near zero in the late 1960s to about 0.12 part per trillion in 1999. It is presently growing by about 0.008 part per trillion per year, or 6% per year. Stratospheric profiles of SF_5CF_3 suggest that it is long-lived in the atmosphere (on the order of 1000 years).

The Kyoto Protocol highlighted the need to assess a broad range of greenhouse gases for their contribution to radiative forcing. Whereas most attention has been placed on the major greenhouse gases (CO_2, CH_4, and N_2O), it is clear that some gases that are present at much lower concentrations can contribute to global warming because of their exceptionally large infrared (IR) absorption. A notable example is SF_6, which is closely chemically related to the "new" molecule SF_5CF_3. SF_6 is of almost exclusively anthropogenic origin, currently present in the atmosphere at only ~4 parts per trillion (ppt), but with a global warming potential (GWP) of 22,200 relative to CO_2 over a 100-year time horizon (1). SF_6 is one of the greenhouse gases that the Kyoto Protocol seeks to control.

We first noted SF_5CF_3 as an unidentified chromatographic peak that eluted shortly after SF_6 in gas chromatography–mass spectrometry (GC-MS) analysis of stratospheric air samples. The identity of the peak was determined by the presence of ions with masses of 68.995 (CF_3^+), 88.967 (SF_3^+), and

126.964 ($SF_5CF_3^+$) in their correct relative abundances, and the identity was then confirmed by an exact GC retention time match with a sample of pure compound (from Flura Corporation, Newport, Tennessee) diluted in nitrogen. The mass spectrum (comprising almost exclusively the three above-mentioned ions) was obtained from the pure compound because no library spectrum could be found.

Air samples were analyzed with the GC-MS system operated in single-ion mode (a mass of 88.967 was used to monitor SF_5CF_3), giving a detection limit of ~1 part per 10^{15} for 800-ml air volumes (2, 3). SF_6 concentrations were referenced to a calibrated ambient air standard (Colorado Mountains, 1994; SF_6 = 3.39 ppt) (4). SF_5CF_3 was calibrated by two separate methods (5), giving a mean concentration in the same air standard of 0.094 ± 0.020 ppt.

Samples of air were pumped out of deep consolidated snow (firn) at Dome Concordia in eastern Antarctica (75°S, 123°E; 3233 m above sea level) in January 1999 (6) at various depths from the surface to pore close-off at ~100 m. Mean equilibration times between changing surface concentrations and air at depth in the firn can be on the order of years or even decades, depending on the diffusivity of the particular gas and its concentration gradient. This was calculated with the aid of a diffusive transport model constrained by measured profiles of gases with well-known atmospheric trends (e.g., CO_2) (7). Profiles of SF_5CF_3 and SF_6 with depth in

the firn are shown in Fig. 1. They are remarkably similar in form, leading to the suspicion that their growth rates are closely related. Published measurements and emission estimates for SF_6 were combined (8) to give the global SF_6 trend shown in the inset of Fig. 1. Modeling this trend gave an excellent match to the observed SF_6 concentrations in the firn, except for a possible slight overestimate from extrapolating the trend from 1997 to 1999. A hypothetical trend for SF_5CF_3 was then constructed with the SF_6 trend scaled to the mean relative concentration of SF_5CF_3 to SF_6 in surface air at Dome Concordia (0.122 to 4.00 ppt) (Fig. 1). This trend was modeled with a diffusion coefficient for SF_5CF_3 in air estimated from molecular volume calculations (9). The resulting fit to the observed SF_5CF_3 profile is very good (Fig. 1), with most measurements falling within an envelope of concentrations 10% above and below the mean. We therefore think that this time trend for SF_5CF_3 is a good representation of its actual atmospheric growth and suggests that emissions began in the late 1950s.

Air was also collected from the stratosphere by using a balloon-borne liquid neon–based cryogenic sampler (10). Vertical profiles of SF_5CF_3 are shown in Fig. 2 for both mid-latitude and Arctic vortex flights, launched from Aire sur l'Adour, France (44°N), and Kiruna, Sweden (68°N), respectively. At both latitudes, the concentrations declined monotonically with altitude. Measurements of SF_6 were used to determine the mean age of air (11) for each sample. The mean ages at maximum altitude were 4 and 7 years for the mid-latitude and Arctic vortex flights, respectively. The greater decline in SF_5CF_3 with altitude observed for the high-latitude flight can be explained by subsidence of older air in the polar vortex. The SF_5CF_3 concentrations expected on the basis of the mean age of air and the atmospheric trend of SF_5CF_3 (from Fig. 1) are shown as thick lines in Fig. 2. Agreement between the predicted and measured SF_5CF_3 is very good within the errors of the measurements, at least at lower altitudes. We therefore expect the upper limit of the lifetime of SF_5CF_3 to approach that of SF_6 [3200 years (12)]. By analogy with SF_6, we do not expect any substantial sinks of SF_5CF_3 in the troposphere nor do we expect uptake by soils, plants, or the ocean (12).

Toward the top of the stratospheric profiles (Fig. 2), there is evidence of a possible divergence toward observed SF_5CF_3 concentrations

[1]School of Environmental Sciences, University of East Anglia, Norwich NR4 7TJ, UK. [2]Ford Motor Company, Mail Drop SRL-3083, Dearborn, MI 48121–2053, USA. [3]Department of Meteorology, University of Reading, Reading RG6 6BB, UK. [4]Institute for Meteorology and Geophysics, Johann Wolfgang Goethe University of Frankfurt, D-60325 Frankfurt, Germany. [5]British Antarctic Survey, Natural Environment Research Council, Cambridge CB3 0ET, UK. [6]Atmospheric Chemistry Division, Max Planck Institute for Chemistry, D-55060 Mainz, Germany.

Fig. 1. Measurements of SF_5CF_3 (triangles) and SF_6 (circles) in air extracted from firn at Dome Concordia, Antarctica, in January 1999 and firn modeling (SF_5CF_3, thick solid line; SF_6, thin solid line) of expected depth profiles based on the atmospheric scenarios shown in the inset. The dotted lines shown for SF_5CF_3 denote concentrations that are ±10% of the modeled line. Error bars on the symbols are 1σ of the total accumulated analytical precision values (the bars are smaller than the symbols for SF_6). The SF_6 trend for 1978 to 1997 was derived from the quadratic fit to measurements made at Cape Grim, Tasmania (8), extrapolated to 1999. To estimate the trend before 1978, we converted global emission estimates of SF_6 from 1953 to 1985 to global average concentrations using SF_6 concentration (ppt) $\approx$ metric tons of $SF_6/25000$ (8). These values were adjusted to equivalent Cape Grim concentrations using the calculated annual growth rate and a time lag of half the interhemispheric exchange time of 1.35 years (17). A third-order polynomial fit to the data yielded SF_6 concentrations for 1953 to 1978.

that are lower than those predicted. This is, however, very sensitive to the accuracy of the reconstructed atmospheric trend and the assumption of a constant SF_5CF_3-to-SF_6 ratio over time (the small offset between measured and predicted concentrations at all altitudes in the later flight suggests some deviation from these assumptions). In the top few kilometers of the profiles, measured N_2O concentrations averaged ~50 parts per billion (ppb). This means that ~80 to 90% of the N_2O that originally entered the stratosphere [~310 ppb in the early

1990s (1)] had been destroyed in this "old" air. If measured SF_5CF_3 concentrations were, on average, 10% lower than those predicted from SF_6, then by analogy to N_2O [lifetime of ~120 years (1)], the stratospheric lifetime of SF_5CF_3 would be on the order of 1000 years. We therefore expect the lifetime of this molecule to be somewhere between several hundred and a few thousand years.

The radiative forcing due to SF_5CF_3 has not previously been evaluated. The IR absorption spectrum of SF_5CF_3, measured over the range from 600 to 3800 cm^{-1} with a Fourier transform IR spectrometer (FTIR), is shown in Fig. 3. IR bands were observed at 755, 884, 889, 903, 1172, and 1257 cm^{-1}. IR absorption increased linearly with SF_5CF_3 concentration. Absorption cross sections (base e, in units of square centimeters per molecule of 7.6 $\times$ 10^{-18} at 903 cm^{-1} and

6.6×10^{-18} at 1257 cm^{-1} and integrated band strengths (units of centimeters per molecule of 1.24 $\times$ 10^{-17} (670 to 780 cm^{-1}), 1.45 $\times$ 10^{-16} (840 to 960 cm^{-1}), and 9.63 $\times$ 10^{-17} (1125 to 1325 cm^{-1}) were derived. These are believed to be accurate to 5% (13). The strength of the IR absorption lines and the fact that 60% of the integrated cross section lies in the atmospheric IR "window" between 800 and 1200 cm^{-1} make SF_5CF_3 a very effective greenhouse gas on a per molecule basis.

Subsequently, the IR absorption spectrum was used to calculate an adjusted cloudy sky radiative forcing (14, 15) of 0.57 W m^{-2} ppb^{-1} for SF_5CF_3. This is the strongest radiative forcing, on a per molecule basis, of any molecule found in the global atmosphere to date (1). Indeed, only one of the more than 100 known or potentially occurring man-made gases surveyed in (1) has a stronger radiative forcing than SF_5CF_3. The forcing due to SF_6 is slightly weaker at 0.52 W m^{-2} ppb^{-1}.

Without better knowledge of the lifetime of SF_5CF_3, it is not possible to calculate the GWP with confidence, but assuming that it has the same lifetime as SF_6, we estimate that its 100-year mass-normalized GWP relative to CO_2 (1) would be 18,000. If the lifetime were 1000 years, the GWP would be only marginally smaller at 17,500. SF_6, which has a slightly higher GWP of 22,200, is the only molecule listed by the World Meteorological Organization/United Nations Environment Programme with a stronger GWP than SF_5CF_3 (1).

It is remarkable that the trends of SF_6 and SF_5CF_3 have tracked each other so closely over the past 30 years. SF_5CF_3 may be a by-product of the manufacture of SF_6, but we have not detected any in a sample of pure SF_6. One of the dominant uses of SF_6 is in gas-insulated switchgear, transformers, accelerators, and other high-voltage equipment.
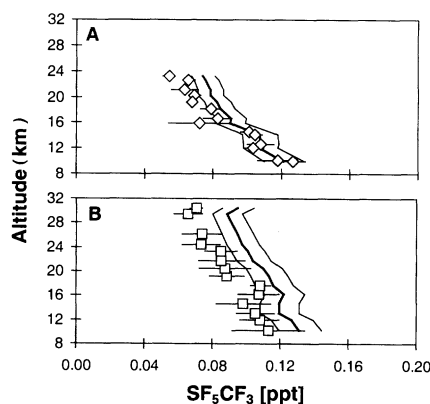
Fig. 2. Measurements of SF_5CF_3 from stratospheric balloon flights launched from **(A)** Kiruna, Sweden (68°N), in February 1997 (diamonds) and **(B)** Aire sur l'Adour, France (44°N), in May 1999 (squares). Error bars are 1σ of the total accumulated analytical precision values. Predicted values are shown as thick lines, based on scaling measured SF_6 concentrations to the constant ratio used to derive the SF_5CF_3 trend in Fig. 1. Because both compounds are growing at essentially the same rate, it is not necessary to correct for nonlinear growth (22). Envelopes of ±10% the predicted concentrations (compare Fig. 1) are shown as thin lines.

Fig. 3. IR spectrum of SF_5CF_3. Samples (from Flura Corporation, Newport, Tennessee) of 0.7 to 3.1 mtorr of SF_5CF_3, purified by repeated freeze-pump-thaw cycling to remove an ~2% SF_6 impurity, were mixed with 700 torr of ultrahigh purity synthetic air (N_2/O_2) and introduced into a 140-liter, 2-m-long, evacuable Pyrex chamber (13). The FTIR was operated at a resolution of 0.5 cm^{-1}, and measurements were made at 296 ± 2 K. σ_e, absorption cross section (base e).
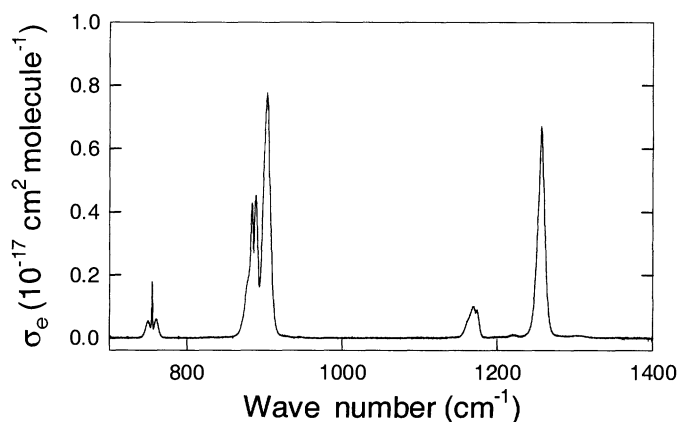
These uses have accounted for an almost constant 80% of SF_6 sales (8); the increasing use by the electronics industry has been largely compensated by the decreasing use in magnesium smelting (8). We speculate that SF_5CF_3 originates as a breakdown product of SF_6 in high-voltage equipment. Such systems likely contain fluoropolymers, which provide a source of CF_3 groups that may be attacked by SF_5 radicals formed by high-voltage discharges.

Despite the large GWP of SF_5CF_3, the amount currently in the atmosphere is so small that the contribution of this molecule to overall radiative forcing is very minor ($<10^{-4}$ W m^{-2}). The present-day burden of SF_5CF_3 is $\sim$3.9 $\times$ 10^3 metric tons, with emissions rising by $\sim$270 metric tons year^{-1} (from the trend shown in Fig. 1 and assuming negligible atmospheric loss). This emission is equivalent in GWP terms (for a 100-year time horizon) to $\sim$1% of the annual UK emission of CO_2 (16). SF_5CF_3, however, has a much longer lifetime than that of CO_2 (atmospheric CO_2 equilibration time of 50 to 200 years), and its rate of growth may be accelerating. There is, therefore, potential for an almost irreversible accumulation of this gas in the atmosphere. SF_5CF_3, unlike CO_2, has no natural sources and therefore has the potential for substantial emission control after its sources have been identified. If it is indeed formed in high-voltage equipment, then there may already be substantial amounts "stored" in electrical installations worldwide. We think that it is important to continue monitoring the atmospheric concentration of SF_5CF_3 in order to determine and control its sources and to guard against an undesirable accumulation of this strong greenhouse gas in the atmosphere.

References and Notes

1. Scientific Assessment of Ozone Depletion: 1998, Global Ozone Research and Monitoring Project, Rep. 44 (World Meteorological Organization, Geneva, 1999).
2. Air samples (200 to 800 ml) were cryofocused at −186°C with liquid argon, desorbed at 90°C, and separated on a temperature-controlled alumina PLOT capillary column. The Micromass "AutoSpec" configuration comprised an electron ionization source, a magnetic field sector, pre– and post–electric field focusing sectors, and a photomultiplier detector.
3. P. J. Fraser, D. E. Oram, C. E. Reeves, S. A. Penkett, A. McCulloch, J. Geophys. Res. 104, 15985 (1999).
4. The air standard was obtained from the U.S. National Oceanic and Atmospheric Administration (NOAA), Boulder, CO. The NOAA scale agrees to within 1% of that of the University of Heidelberg, Heidelberg, Germany (1, 17).
5. First, pure SF_5CF_3 (Flura Corporation, Newport, TN) was successively diluted in large stirred aluminum drums to 1 part per billion by volume, followed by injection of microliter amounts into the GC-MS using a small sample loop filled to varying pressures to span the range of concentrations that we measured in ambient air. These measurements were referenced to a synthetic calibrated 10-ppb SF_6-in-nitrogen standard ["Heidelberg" scale (17)] that was prepared and analyzed in the same way. Second, the relative abundances of two ions common to both SF_6 and SF_5CF_3 (masses of 89 and 127) were determined from full-scan mass spectra of diluted pure gases and compared with the relative peak areas in the NOAA standard. The second method is independent of errors arising from dilution effects, but it assumes invariant ionization efficiency. The first method yielded a concentration in the NOAA standard (collected at Niwot Ridge, CO, in spring 1994) of 0.072 ± 0.009 ppt, whereas the second method gave a concentration of 0.116 ± 0.018 ppt.
6. Air was extracted by drilling a bore hole to successive depths, each time letting down an inflatable sleeve to seal off the hole near the bottom, and then pumping air out from beneath the seal (18) into fused silica-lined stainless steel sample flasks (SilcoCan canisters, Restek Corporation, Bellefonte, PA). Integrity of the pumped air was assured by continuous in situ monitoring of CO_2.
7. A. Fabre, J.-M. Barnola, L. Arnaud, J. Chappellaz, Geophys. Res. Lett. 27, 557 (2000).
8. M. Maiss and C. A. M. Brenninkmeijer, Environ. Sci. Technol. 32, 3077 (1998).
9. E. N. Fuller, P. D. Schettler, J. C. Giddings, Ind. Eng. Chem. 58, 19 (1966).
10. A. Engel, U. Schmidt, R. A. Stachnik, J. Atmos. Chem. 27, 107 (1997).
11. M. Strunk et al., Geophys. Res. Lett. 27, 341 (2000).
12. A. R. Ravishankara, S. Solomon, A. A. Turnipseed, R. F. Warren, Science 259, 194 (1993).
13. S. Pinnock, M. D. Hurley, K. P. Shine, T. J. Wallington, T. J. Smyth, J. Geophys. Res. 100, 23227 (1995).
14. Intergovernmental Panel on Climate Change, Climate Change 1995: The Science of Climate Change, J. T. Houghton et al., Eds. (Cambridge Univ. Press, Cambridge, 1996).
15. The radiative forcing was calculated with a 10 cm^{-1} narrow band radiation scheme in which the SF_5CF_3 forcing was calibrated to agree exactly with line-by-line calculations [using an irradiance version of the Reference Forward Model (19)] for clear skies (20). Well-mixed vertical profiles were assumed, and the global-mean forcing was derived by averaging three profiles representing the tropics and extratropics (21).
16. J. W. L. Goodwin, A. G. Salway, T. P. Murrels, C. J. Dore, H. S. Eggleston, UK Emissions of Air Pollutants 1970–1997: A Report of the National Atmospheric Emissions Inventory (AEA Technology, Harwell, UK, 1999).
17. M. Maiss and I. Levin, Geophys. Res. Lett. 21, 569 (1994).
18. J. Schwander et al., J. Geophys. Res. 98, 2831 (1993).
19. A. Dudhia, Reference Forward Model v3 Software User's Manual, ESA Document PO-MA-OXF-GS-0003 (Department of Atmospheric, Oceanic and Planetary Physics, University of Oxford, Oxford, 1997).
20. N. Christidis, M. D. Hurley, S. Pinnock, K. P. Shine, T. J. Wallington, J. Geophys. Res. 102, 19597 (1997).
21. R. S. Freckleton et al., Q. J. R. Meteorol. Soc. 124, 2099 (1998).
22. C. M. Volk et al., J. Geophys. Res. 102, 25543 (1997).
23. This work was supported by the European Commission (EC) through the FIRETRACC/100 (Firn Record of Trace Gases Relevant to Atmospheric Chemical Change over 100 Years) and HALOMAX (Mid- and High-Latitude Stratospheric Distribution of Long- and Short-lived Halogen Species During the Maximum of the Chlorine Loading) projects; by the UK Natural Environment Research Council; and by the UK Department of the Environment, Transport and the Regions. The Antarctic field work was also supported by the European Science Foundation/EC European Project for Ice Coring in Antarctica (EPICA) program, by the French Polar Institute, and by the Ente per le Nuove Tecnologie, l'Energia e l'Ambiente (ENEA) Antarctic Project (Italy). We particularly thank L. Arnaud and A. Manouvrier [CNRS–Laboratoire de Glaciologie et de Géophysique de l'Environnement (LGGE)] for firn sampling, H. McIntyre (University of East Anglia, Norwich, UK) for GC-MS analyses, and J. Chappellaz and J.-M. Barnola (CNRS-LGGE) for the firn model and supporting data.

7 March 2000; accepted 9 June 2000

CLAVATA3, a Multimeric Ligand for the CLAVATA1 Receptor-Kinase

Amy E. Trotochaud, Sangho Jeong, Steven E. Clark*

The CLAVATA1 (CLV1) and CLAVATA3 (CLV3) proteins form a potential receptor and ligand pair that regulates the balance between cell proliferation and differentiation at the shoot meristem of Arabidopsis. CLV1 encodes a receptor-kinase, and CLV3 encodes a predicted small, secreted polypeptide. We demonstrate that the CLV3 and CLV1 proteins coimmunoprecipitate in vivo, that yeast cells expressing CLV1 and CLV2 bind to CLV3 from plant extracts, and that binding requires CLV1 kinase activity. CLV3 only associates with the presumed active CLV1 protein complex in vivo. More than 75% of CLV3 in cauliflower extracts is bound with CLV1, consistent with hypotheses of ligand sequestration. Soluble CLV3 was found in an approximately 25-kilodalton multimeric complex.

Although several biologically active putative ligands and putative receptors have been identified in plants (1), no proteinaceous ligand and cognate receptor pair have been identified at present. The CLV1 and CLV3 gene products are likely candidates for such a pair. The CLV1 and CLV3 genes function in the same pathway, and clv1 and clv3 mutations exhibit dominant interactions (2). CLV1 encodes a predicted receptor-like protein kinase with an extracellular domain composed of 21 tandem leucine-rich repeats (LRRs) and an intracellular protein kinase domain that has been shown to act as a serine kinase (3–5). CLV3 encodes a predicted small, secreted protein (6).

Department of Biology, University of Michigan, Ann Arbor, MI 48109–1048, USA.

*To whom correspondence should be addressed. E-mail: clarks@umich.edu