

First measurements of CFC-113 and HCFC-142b from space using ACE-FTS infrared spectra

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Received 12 January 2005; revised 21 February 2005; accepted 15 April 2005; published 4 June 2005.

[1] The first measurements of CFC-113 ($\text{CCl}_2\text{FCClF}_2$) and HCFC-142b (CH_3CClF_2) from space have been performed by the Atmospheric Chemistry Experiment (ACE), a satellite-based mission for remote sensing of the Earth's atmosphere. Retrievals for the volume mixing ratio profiles of these two molecules have been performed for ACE-FTS measurements at mid-latitudes and in the tropics, and the results are compared with AGAGE surface measurements. The agreement between ACE and AGAGE mixing ratios is within 15% for both CFC-113 and HCFC-142b.

Citation: Dufour, G., C. D. Boone, and P. F. Bernath (2005), First measurements of CFC-113 and HCFC-142b from space using ACE-FTS infrared spectra, *Geophys. Res. Lett.*, 32, L15S09, doi:10.1029/2005GL022422.

1. Introduction

[2] Chlorofluorocarbons (CFCs) play a key role in the depletion of stratospheric ozone and have a strong global warming potential (GWP) [*World Meteorological Organization (WMO)*, 1999; *Montzka et al.*, 2003; *Intergovernmental Panel on Climate Change*, 2001]. The regulation of CFC emissions by the Montreal Protocol and its amendments has mitigated their environmental impact: tropospheric mixing ratios of CFC-11 (CCl_3F) and CFC-113 ($\text{CCl}_2\text{FCClF}_2$) have been decreasing since 1996, and the rate of increase for CFC-12 (CCl_2F_2) mixing ratios has slowed significantly [*Montzka et al.*, 2003]. Conversely, CFC substitutes, the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs), are increasing rapidly [*O'Doherty et al.*, 2004; *Prinn et al.*, 2000; *Montzka et al.*, 2003] and thus play an increasingly important role in climate change. Although their ozone depletion potential is very low [*Montzka et al.*, 2003], CFC substitutes can have a significant contribution to the atmospheric chlorine loading [*Schauffler et al.*, 2003] and their global warming potential is high.

[3] The two most abundant CFCs (CFC-11 and CFC-12) and the most abundant HCFC (CHClF₂, named HCFC-22) have been extensively studied since the mid 1980s. Ground-based [see, e.g., *Zander et al.*, 1983; *Sherlock et al.*, 1997], airborne [e.g., *Toon et al.*, 1999; *Blake et al.*, 1996; *Elkins et al.*, 1996], balloon-borne [e.g., *Sen et al.*, 1999; *Engel et al.*, 1998], and space-borne [e.g., *Khosrawi et al.*, 2004; *Hoffman et al.*, 2004] measurements are regularly performed. The majority of information on the less abundant CFCs, HCFCs, and HFCs is provided by in situ and ground-based remote measurements through two global measurement

networks – the ALE/GAGE/AGAGE network [*Prinn et al.*, 2000] and the NOAA/CMDL network [*Hall et al.*, 2002], where the measurement techniques employed are gas chromatography-mass spectrometry (GC-MS) and gas chromatography with electron capture detection (GC-ECD). Gas chromatography measurements have also been reported from in situ sampling in the upper troposphere and lower stratosphere [e.g., *Schauffler et al.*, 1993, 2003; *Toon et al.*, 1999]. CFC-113 has been measured from a balloon-borne Fourier transform spectrometer [*Sen et al.*, 1999], but no space-borne measurements have been reported.

[4] We report the first satellite-based measurements of CFC-113 and HCFC-142b (CH_3CClF_2), the third and the second most abundant CFC and HCFC, respectively. The volume mixing ratio profiles are retrieved from solar occultation spectra recorded by the high resolution (0.02 cm^{-1}) infrared Fourier transform spectrometer (ACE-FTS) on-board the ACE satellite, launched the 12 August 2003 and fully operational since January 2004 [*Bernath et al.*, 2005].

2. Results and Discussion

[5] The signal-to-noise ratio (SNR) of ACE-FTS spectra is higher than 300:1 over a large portion ($1000\text{--}3000\text{ cm}^{-1}$) of the spectral range covered ($750\text{--}4400\text{ cm}^{-1}$). The residual non-linearity in the transmission spectra is very low because of the use of photovoltaic HgCdTe and InSb detectors. This level of performance permits the retrieval of very weak absorbers. The presence of a CFC-113 absorption band in the ATMOS [*Gunson et al.*, 1996] spectra between 810 and 830 cm^{-1} was previously noted by *Coheur et al.* [2003]. The residuals for an ACE-FTS measurement in this spectral region with and without the inclusion of CFC-113 are shown in Figure 1. The calculated absorption of CFC-113 is added in the figure for comparison. Although very weak, there is a clear signature from the molecule in the spectrum. *Coheur et al.* [2003] have underlined that CFC-113 would be difficult to retrieve from ATMOS spectra due to the poor signal-to-noise ratio of ATMOS spectra in this region (around 5:1). ATMOS also used a photoconductive HgCdTe detector, which resulted in a large residual non-linearity (i.e., after correction) of several percent in the spectra. The higher quality of ACE-FTS spectra, even in this unfavorable region (SNR around 100:1), permits the retrieval of CFC-113.

[6] Several other absorption bands of CFC-113 are also visible in ACE-FTS spectra, around 900 cm^{-1} , 1120 cm^{-1} and 1180 cm^{-1} . For the retrieval, we use the two following windows: $800\text{--}830\text{ cm}^{-1}$, and $1116\text{--}1122\text{ cm}^{-1}$. The main interferers are H_2O , CO_2 , O_3 , and HCFC-22 for the first

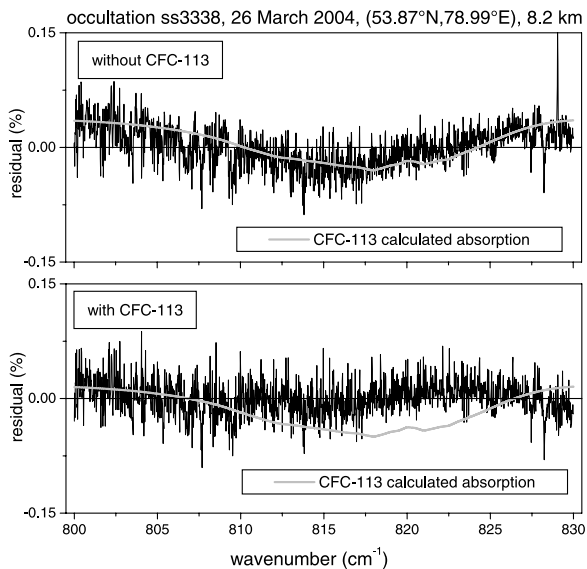


Figure 1. In the top panel, the residuals (observed-calculated) are plotted without including CFC-113 absorption. In the lower panel is the plot of the residuals when CFC-113 absorption is included. Both panels show the computed contribution of CFC-113 using the vmr retrieved for this spectrum.

one, and H_2O , O_3 , N_2O , and CH_4 for the second one. Volume mixing ratio profiles for the interfering species are retrieved simultaneously with the target molecule, using a global fit approach coupled with a Levenberg-Marquardt non-linear least squares method (C. D. Boone et al., Applied Optics, manuscript in preparation, 2005). The results are obtained from the version 1.0 of the retrieval algorithm using the ATMOS linelist for the interferers and the HITRAN2004 [Rothman et al., 2005] cross sections for the target species.

[7] Eight midlatitude occultations recorded around 53°N on 26 and 27 March 2004, as well as ten occultations recorded in the tropics (25°S – 25°N) between 31 January and 8 February 2004 have been analyzed. Retrievals for CFC-113 extended from 8 to 15 km in altitude. For the occultations near 53°N , Figure 2 shows the retrieval results for this molecule. The errors given for the mean profile correspond to statistical 1σ -errors and are probably underestimated. For balloon-borne spectroscopic measurements of CFC-113, Sen et al. [1999] considered the errors to be at least 20% to account for the spectroscopic parameter accuracy, a source of uncertainty that has not been completely accounted for by our error bars (especially when they are smaller than 20%). Moreover, only 6 cross section measurements at different temperatures are available for each spectral region from the HITRAN database [Rothman et al., 2005], so few that the interpolation of cross sections as a function of temperature could be compromised in accuracy. However, the individual profiles are consistent, and the scatter is relatively small. The CFC-113 mixing ratio values measured by the ACE-FTS are also compared in Figure 2 to in situ measurements, taken as the mean value of the monthly averages from January to March 2004 reported by the AGAGE station in Mace Head, Ireland

(data available at http://cdiac.ornl.gov/ftp/ale_gage_Agage/AGAGE/). The difference between the mean ACE-FTS and the AGAGE values is less than 5% on average for the midlatitude measurements in Figure 2 and less than 10% for the tropical measurements.

[8] Coheur et al. [2003] projected that the ACE-FTS instrument would be able to detect HCFC-142b starting in about 2005, but the atmospheric concentration of the molecule was high enough to detect it in early 2004. Two sharp spectral features of HCFC-142b are clearly visible in the ACE-FTS residuals. We have used these two strong features to retrieve HCFC-142b vertical profiles up to 19 km.

[9] The analysis set consisted of 12 midlatitude occultations recorded around 53°N on 26 and 27 March 2004, along with 5 occultations recorded in the tropics (25°S – 25°N) between 31 January and 8 February 2004. The two microwindows selected for this molecule are: 1132.5 – 1136.5 cm^{-1} and 1191.5 – 1195.5 cm^{-1} . The latter is somewhat broader than the microwindow suggested by Coheur et al. [2003]. The main interferers are H_2O , O_3 , CH_4 , and N_2O for the first microwindow, and H_2O , O_3 , CH_4 , and N_2O for the second microwindow. Figure 3 shows the HCFC-142b midlatitude retrieval results. As before, the errors correspond to 1σ statistical fitting errors. For this molecule, only 3 cross section measurements at different temperatures are available in the HITRAN database, once again leading to questionable accuracy for interpolation to cover the relatively broad range of temperatures encountered in atmospheric remote sensing. The lack of cross sections is likely the main source of errors for the HCFC-142b retrieval. However, the consistency between individual measurements is reasonably good. Moreover, the mean profile at 53°N agrees well with the mean value from the AGAGE station in Mace Head, Ireland. The difference between the mean ACE-FTS and the AGAGE values is less

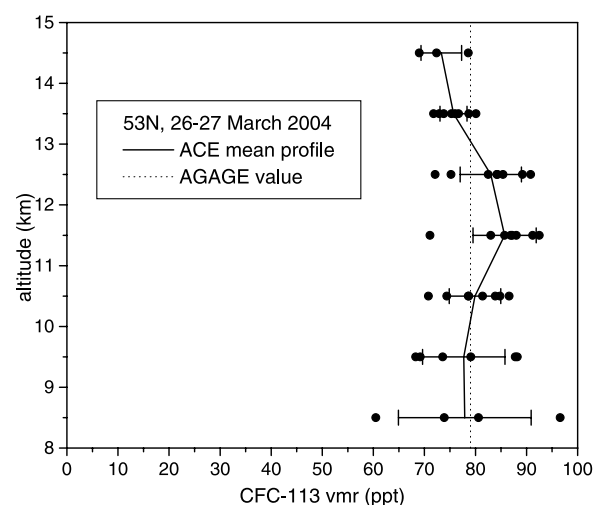


Figure 2. Individual profiles (circles) of CFC-113 and the corresponding mean profile (line) measured by ACE-FTS on 26–27 March 2004 near 53°N are compared to the 2004 mean mixing ratio value (dotted line) of the available monthly averages measured at the AGAGE station, Mace Head (53°N , 10°W), Ireland.

than 10% on average for these midlatitude measurements and less than 15% for tropical measurements.

[10] Because of their long lifetime and low reactivity in the atmosphere [Prinn *et al.*, 2000], CFC-113 and HCFC-142b should be well-mixed and have similar concentrations at different locations within a hemisphere, although comparing measurements from the two hemispheres has shown significant differences [Fraser *et al.*, 1996; O'Doherty *et al.*, 2004]. For instance, O'Doherty *et al.* [2004] have reported a difference of around 2.5 ppt for HCFC-142b between the two hemispheres. The current accuracy of our measurements would not allow us to distinguish such a small difference, but perhaps further analysis of other occultations will give us the statistics to address this issue.

[11] For now, we test the consistency of results for two different geographical regions within a hemisphere (midlatitude and tropical) for both CFC-113 and HCFC-142b. The results are shown in Figure 4. The profiles for the different geographical regions agree well, to the accuracy of our results (i.e., the 1 σ -error bars overlap, neglecting the highest altitude results for HCFC-142b). The January–March 2004 AGAGE value at 53°N is added for comparison. The CFC-113 tropical profile tends to be smaller than the AGAGE value and the midlatitude profile for all altitudes. Using occultations measured in the both hemispheres to calculate the mean tropical profile could contribute to this bias; however, another contribution could arise from the higher levels of water vapor in the tropics, which could disturb the retrieval process for a weak absorber like CFC-113. Concerning HCFC-142b, the retrieval is likely less accurate than for CFC-113 (because of a weaker contribution to the spectrum and fewer cross sections), so it is perhaps early to draw conclusions on systematic differences.

3. Conclusions

[12] For the first time, CFC-113 (CCl₂FCClF₂) and HCFC-142b (CH₃CClF₂) have been measured with a

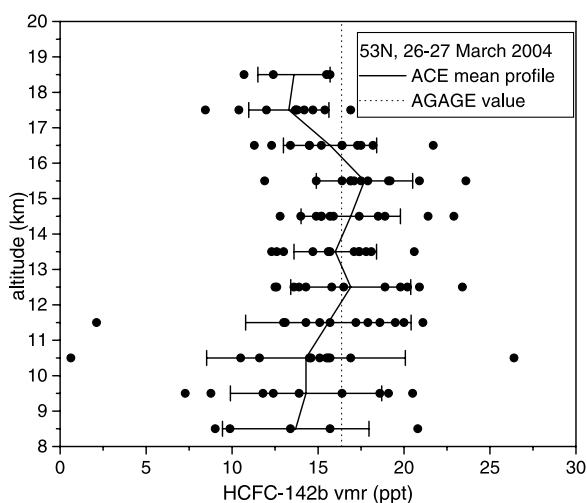


Figure 3. Individual profiles (circles) of HCFC-142b and the corresponding mean profile (line) measured by ACE-FTS on 26–27 March 2004 near 53°N are compared to the 2004 mean mixing ratio value (dotted line) of the available monthly averages measured at the AGAGE station, Mace Head (53°N, 10°W), Ireland.

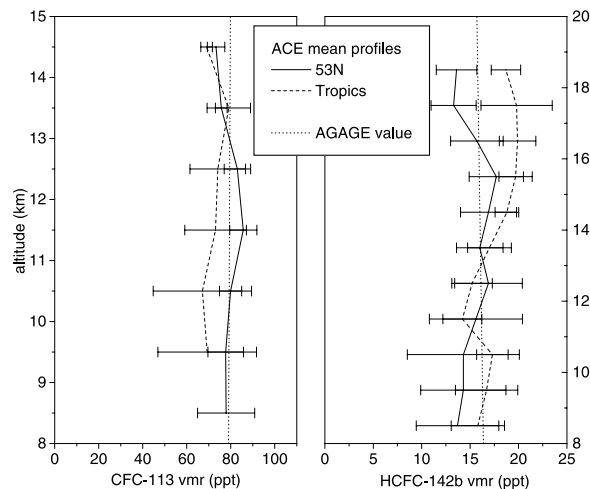


Figure 4. Comparison between the midlatitude and the tropical mean profiles of CFC-113 (left) and HCFC-142b (right).

space-borne infrared spectrometer. We have demonstrated the capabilities of the ACE-FTS instrument for measuring their vertical profiles in the upper troposphere and lower stratosphere. The ACE-FTS profiles are consistent with the surface values of CFC-113 and HCFC-142b measured by AGAGE. A major limitation for our retrievals is the lack of cross section measurements. Further studies are needed to improve the quality and the accuracy of the profiles as well as to see if the ACE-FTS instrument can capture the geographical and temporal variations of CFC-113 and HCFC-142b. In any case, even if the accuracy is worse than in situ measurements, ACE measurements of CFC-113 and HCFC-142b (with further work) will provide complementary data to the ALE/GAGE/AGAGE and NOAA/CMDL surface networks and airborne measurements: our vertical profiles in the free troposphere and in the lower stratosphere will provide extended spatial coverage and good temporal coverage to follow long-term trends.

[13] **Acknowledgments.** Funding for ACE is provided by the Canadian Space Agency and the Natural Sciences and Engineering Research (NSERC) of Canada. Support was also provided by the NSERC-Bomem-CSA-MS-C Industrial Research Chair in Fourier Transform Spectroscopy.

References

- Bernath, P. F., *et al.* (2005), Atmospheric Chemistry Experiment (ACE): Mission overview, *Geophys. Res. Lett.*, **32**, L15S01, doi:10.1029/2005GL022386.
- Blake, D. R., *et al.* (1996), Three-dimensional distribution of nonmethane hydrocarbons and halocarbons over the northwestern Pacific during the 1991 Pacific Exploratory Mission (PEM-West A), *J. Geophys. Res.*, **101**, 1763–1778.
- Coeur, P. F., C. Clerbaux, and R. Colin (2003), Spectroscopic measurements of halocarbons and hydrohalocarbons by satellite-borne remote sensors, *J. Geophys. Res.*, **108**(D4), 4130, doi:10.1029/2002JD002649.
- Elkins, J. W., *et al.* (1996), Airborne gas chromatograph for in situ measurements of long-lived species in the upper troposphere and lower stratosphere, *Geophys. Res. Lett.*, **23**, 347–350.
- Engel, A., U. Schmidt, and D. McKenna (1998), Stratospheric trends of CFC-12 over the past two decades: Recent observational evidence of declining growth rates, *Geophys. Res. Lett.*, **25**, 3319–3322.
- Fraser, P., *et al.* (1996), Lifetime and emission estimates of 1,1,2-trichlorotrifluoroethane (CFC-113) from daily global background observations June 1982–June 1994, *J. Geophys. Res.*, **101**, 12,585–12,599.

- Gunson, M. R., et al. (1996), The Atmospheric Trace Molecule Spectroscopy (ATMOS) Experiment: Deployment on the ATLAS Space Shuttle missions, *Geophys. Res. Lett.*, *23*, 2333–2336.
- Hall, B. D., et al. (2002), Halocarbons and other atmospheric trace species, in *Climate Monitoring and Diagnostics Laboratory: Summary Report No. 26, 2000–2001*, edited by D. B. King and C. R. Schnell, pp. 106–135, NOAA/Clim. Monit. and Diagnostics Lab., Boulder, Colo.
- Hoffmann, L., R. Spang, and M. Riese (2004), Retrieval of chlorofluorocarbon distributions from Envisat MIPAS measurements, *Proc. SPIE Int. Soc. Opt. Eng.*, *5571*, 193–204.
- Intergovernmental Panel on Climate Change (IPCC) (2001), *Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. T. Houghton et al., 881 pp., Cambridge Univ. Press, New York.
- Khosrawi, F., et al. (2004), Validation of CFC-12 measurements from the Improved Limb Atmospheric Spectrometer (ILAS) with the version 6.0 retrieval algorithm, *J. Geophys. Res.*, *109*, D06311, doi:10.1029/2003JD004325.
- Montzka, S. A., et al. (2003), Controlled substances and other source gases, in *Scientific Assessment of Ozone Depletion: 2002, Global Ozone Res. Monit. Proj. Rep. 47*, chap. 1, pp. 1.1–1.83, World Meteorol. Org., Geneva.
- O'Doherty, S., et al. (2004), Rapid growth of hydrofluorocarbon 134a and hydrochlorofluorocarbons 141b, 142b and 22 from Advanced Atmospheric Gases Experiment (AGAGE) observations at Cape Grim, Tasmania, and Mace Head, Ireland, *J. Geophys. Res.*, *109*, D06310, doi:10.1029/2003JD004277.
- Prinn, R. G., et al. (2000), A history of chemically and radiatively important gases in air deduced from ALE/GAGE/AGAGE, *J. Geophys. Res.*, *105*, 17,751–17,792.
- Rothman, L. S., et al. (2005), The HITRAN 2004 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Transfer*, in press.
- Schauffler, S. M., et al. (1993), Measurements of halogenated compounds near the tropical tropopause, *Geophys. Res. Lett.*, *20*, 2567–2570.
- Schauffler, S. M., et al. (2003), Chlorine budget and partitioning during the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE), *J. Geophys. Res.*, *108*(D5), 4173, doi:10.1029/2001JD002040.
- Sen, B., et al. (1999), The budget and partitioning of stratospheric chlorine during the 1997 Arctic summer, *J. Geophys. Res.*, *104*, 26,653–26,665.
- Sherlock, V. J., et al. (1997), Increase in the vertical column abundance of HCFC-22 (CHClF₂) above Lauder, New Zealand, between 1985 and 1994, *J. Geophys. Res.*, *102*, 8861–8866.
- Toon, G. C., et al. (1999), Comparison of MkIV balloon and ER-2 aircraft measurements of atmospheric trace gases, *J. Geophys. Res.*, *104*, 26,779–26,790.
- World Meteorological Organization (1999), *Scientific Assessment of Ozone Depletion: 1998*, Geneva.
- Zander, R., G. M. Stokes, and J. W. Brault (1983), Simultaneous detection of FC-11, FC-12 and FC-22 through 8 to 13 micrometers IR solar observations from the ground, *Geophys. Res. Lett.*, *10*, 521–524.

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