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First remote sensing observations of trifluoromethane (HFC-23) in the upper troposphere and lower stratosphere

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[1] This work reports the first remote sensing measurements of atmospheric HFC-23 (CHF₃) using solar occultation measurements made by the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS) and the Jet Propulsion Laboratory Mark IV (MkIV) balloon interferometer. A total of 8809 ACE occultations measured between 2004 and 2010 have been processed, along with 24 MkIV occultations measured between 1989 and 2007. ACE data (yearly averages over the 10–25 km altitude range) in the tropics/subtropics (40°S–40°N) reveal a trend of $4.0 \pm 1.6\%$ per year in the growth of HFC-23 for 2004–2009 (or $3.9 \pm 1.2\%$ per year for 2004–2010), slightly smaller than surface measurements from Cape Grim air archive samples over the same time period ($4.7 \pm 0.3\%$ per year). The northern midlatitude and high-latitude MkIV data (averaged over the 10–25 km altitude range) indicate a growth rate of $5.8 \pm 0.3\%$ per year over the period 1989–2007 ($5.3 \pm 0.4\%$ per year for just the midlatitude data), similar to the Cape Grim surface trend of $5.7 \pm 0.1\%$ per year over the same period. The absolute HFC-23 volume mixing ratios measured by ACE and MkIV in the upper troposphere/lower stratosphere are in good agreement (<5% bias) with each other but are ~30% larger than ground-based measurements. The source of this bias has not been definitively ascertained; however, spectroscopic errors are the most likely cause.

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1. Introduction

[2] The success of the Montreal Protocol [*United Nations Environment Programme*, 1996] in phasing out ozone-depleting substances (ODSs), principally the chlorofluorocarbons (CFCs), has resulted in the development and commercialization of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) as replacements. Under the Montreal Protocol, HCFCs, which have low-ozone-depletion potentials, are classified as “transitional substitutes” and will be fully phased out by 2020 for developed countries, and by 2030 for developing countries. A small percentage of these molecules will still be used for servicing purposes until 2040.

[3] Increasingly, the demand for refrigeration, air conditioning, and thermal-insulating foam products is being met by HFCs, which are not restricted by the Montreal Protocol.

HFCs do not deplete the ozone layer but are powerful greenhouse gases (along with CFCs and HCFCs) with global warming potentials (GWPs) many times greater than CO₂. The primary emissions of trifluoromethane (CHF₃, HFC-23), however, do not arise through its use as an ODS replacement, but as a byproduct (overfluorination of chloroform) during the production of HCFC-22 (CHClF₂). HFC-23 emissions from semiconductor etching, and refrigeration and fire extinguisher losses are relatively small. HFC-23 was the first HFC to be measured in the atmosphere, using flask samples dating back to 1978 from Cape Grim (Tasmania, Australia) [*Oram et al.*, 1998] and Cape Mearns (Oregon, USA) [*Culbertson et al.*, 2004]. In the early 2000s, HFC-23 was overtaken as the most abundant HFC in the atmosphere by HFC-134a (CH₂FCF₃), a direct consequence of the rapid growth in the use of HFCs as ODS replacements since the 1990s.

[4] HFC-23 has a long atmospheric lifetime of 222 years [*Montzka et al.*, 2011] and a 100 year GWP of 14,200 [*Daniel et al.*, 2011], meaning that continued HFC-23 emissions will significantly contribute to climate forcing. During the period 2006–2008, the GWP-weighted emissions of HFC-23 contributed ~0.2 Gt CO₂-equivalent/year (eq./yr) [*Montzka et al.*, 2011], slightly higher than the value of 0.18 Gt CO₂-eq./yr inferred from the data of *Miller et al.* [2010] over the same time period. The sum of all other HFC

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emissions increased by 8–9%/yr from 2004 to 2008, reaching 0.39 Gt CO₂-eq./yr by 2008 [Montzka *et al.*, 2010].

[5] HFC-23 has attracted media coverage [Tollefson, 2010] in recent years owing to its association with Clean Development Mechanism (CDM) climate change mitigation projects, and mounting calls to incorporate the regulation and phase down of HFCs into the Montreal Protocol, which has been so successful in phasing out CFCs and has unintentionally contributed to mitigating climate change [Daniel *et al.*, 2011]. The CDM, which is administered under the UN Framework Convention on Climate Change and its principal update, the Kyoto Protocol, is a mechanism that allows emission-reduction projects in developing countries to earn certified emission reduction (CER) credits, each equivalent to one tonne of CO₂. These CERs can be traded and sold, and used by industrialized countries to meet a part of their emission reduction targets under the Kyoto Protocol. The costs for destroying HFC-23 are below U.S.\$1/tCO₂-eq., whereas the market price of CERs is considerably higher (~U.S.\$10 as of November 2011). As explained by Schneider [2011], there are “perverse incentives” for project operators to maintain high ratios of HFC-23 byproduct to HCFC-22 production, and even to overproduce HCFC-22, simply to maximize HFC-23 formation and destruction, undermining the HCFC phase out under the Montreal Protocol. It is currently possible for such companies to make more money destroying excess HFC-23 than selling HCFC-22. In 2011 the European Union banned the use of HFC-23 credits in its emissions-trading system from May 2013 (European Commission, 2011, http://ec.europa.eu/clima/documentation/ets/docs/linking/qualityreg_en.pdf).

[6] HFCs have no natural sources. Their atmospheric abundances can be explained only by anthropogenic emissions [Montzka *et al.*, 2011]. Most atmospheric measurements of HFCs have been made in situ with ground-based instruments, for example, the Advanced Global Atmospheric Gases Experiment (AGAGE, 2011, <http://agage.eas.gatech.edu/>). Increasingly, satellite instruments are now able to detect these molecules. For example, Nassar *et al.* [2006] measured HFC-134a (CH₂FCF₃) using data from the Atmospheric Chemistry Experiment Fourier transform spectrometer (ACE-FTS), on board SCISAT-1 [Bernath *et al.*, 2005]. This was the first detection from orbit of an HFC in the atmosphere.

[7] This paper outlines the first remote sensing and the first global satellite based measurements of HFC-23 in the atmosphere. ACE-FTS and balloon-borne Mark IV (MkIV)-FTS observations are presented. Trends in HFC-23 in the upper troposphere/lower stratosphere (UTLS) derived from these observations are compared with ground-based measurements.

2. Infrared Spectroscopy of HFC-23

[8] The retrieval of HFC-23 volume mixing ratios (VMRs) from ACE and MkIV atmospheric measurements requires spectroscopic information from laboratory HFC-23 absorption spectra. The HFC-23 spectroscopic data employed in the retrievals described here are a set of pseudolines covering 1100 to 1240 cm⁻¹, derived from laboratory spectra recorded by Chung [2005]. Pseudolines are “effective” spectral lines that empirically reproduce the

pressure and temperature dependencies of spectral absorption, without any recourse to quantum-mechanical assignments. They are a convenient means of interpolating (and extrapolating) cross sections such that the derived absorption varies smoothly with temperature and pressure (and hence altitude). The HFC-23 pseudolines and further information on their derivation can be found at the JPL MkIV Web site (<http://mark4sun.jpl.nasa.gov/pseudo.html>).

[9] The Chung spectra were recorded at a resolution of 0.02 cm⁻¹ at temperatures from 214 to 300 K and N₂-broadening pressures from 0 to 253 Torr. They suffer from some problems; the pure spectra are slightly under-resolved and there appear to be inconsistencies in some of the tabulated HFC-23 partial pressures. This latter problem was remedied by adjusting the assumed absorber amounts to bring them into line with each other and with three composite spectra taken from the Pacific Northwest National Laboratory (PNNL) IR database [Sharpe *et al.*, 2004]. These spectra were recorded at poorer resolution (0.112 cm⁻¹) as mixtures with pure N₂ gas at pressures of 760 Torr and temperatures of 278, 293, and 323 K, making them inappropriate for remote sensing of the UTLS (temperature and pressure too high), or for pseudo line list generation (too poor resolution). However, they are useful for calibrating band intensities since they are determined from multiple path length–concentration burdens, and great care has been taken to ensure that sample concentrations have been determined accurately. Additionally, this calibration assumes that the integrated band intensities are independent of temperature, which is true for isolated bands comprising primarily fundamentals. This technique has been used by some of the present authors in previous quantitative spectroscopic measurements [e.g., Harrison *et al.*, 2011a, 2011b].

[10] The resulting pseudo line list gives integrated band intensities that agree with the three PNNL HFC-23 spectra to within 0.5%. Statistical errors for these three spectra range from 0.13–0.47%, with systematic errors estimated as ≤3%. Fits of the pseudolines to the measured laboratory spectra produced fitting residuals as high as 4% rms, which could point to an inconsistency in the recorded pressures and temperatures. However, when the pseudolines are used to retrieve abundances from the three PNNL spectra, the results are consistent to better than 0.2%.

3. HFC-23 Retrievals

3.1. ACE-FTS

[11] The ACE-FTS uses the sun as a light source to record atmospheric limb transmittance spectra during sunrise and sunset (“solar occultation”). The resulting spectra, with high signal-to-noise ratios, are recorded through long atmospheric limb paths (~300 km effective length), thus providing a low detection threshold for trace species. The ACE-FTS is a high-resolution (0.02 cm⁻¹) instrument that covers the spectral region from 750 to 4400 cm⁻¹. ACE has an excellent vertical resolution of about 2–3 km in the troposphere and can measure up to 30 occultations (i.e., sunrise and sunset events viewed from the orbiting satellite) per day, with each occultation sampling the atmosphere from 150 km down to the cloud tops (or 5 km in the absence of clouds). The locations of ACE occultations are dictated by the 650 km altitude, 74° inclination circular orbit of the SCISAT-1

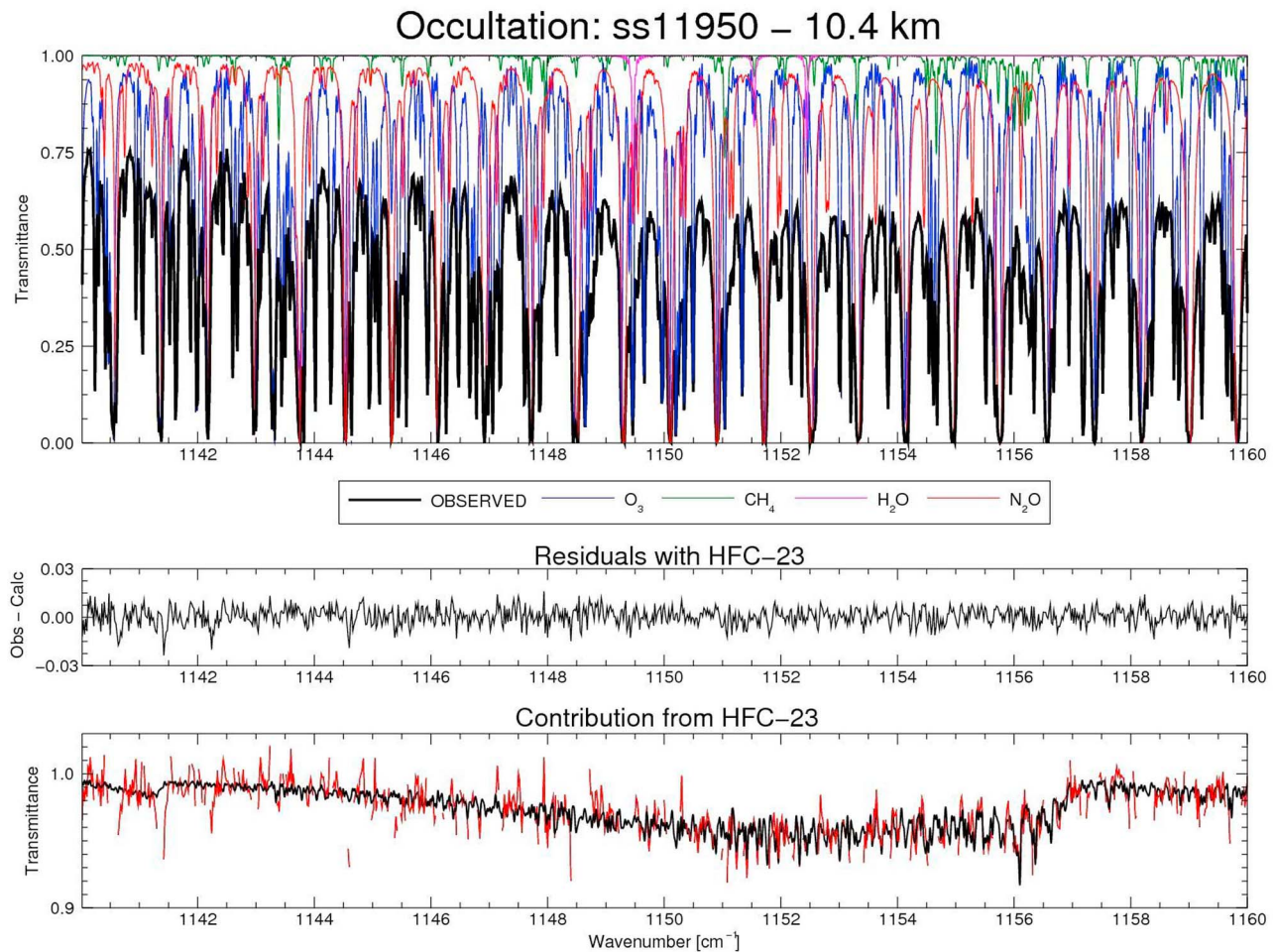


Figure 1. (top) The transmittance spectrum for a single measurement from ACE occultation ss11950 at a tangent height of 10.4 km. Also shown are contributions due to absorption of N_2O , O_3 , CH_4 , and H_2O (contributions from all isotopologues). (middle) Observed – calculated residuals for the retrieval. (bottom) HFC-23 contribution, determined from the ratio of the measured ACE spectrum to the calculated spectrum (for all absorbers except HFC-23); transmittances below 0.3 were filtered out in order to suppress the large contributions from saturated lines. Overlaid on this (in black) is the calculated contribution of HFC-23 absorption for this measurement (about 4%).

satellite and the relative position of the sun. Over the course of a year, the ACE-FTS records atmospheric spectra over a large portion of the globe [Bernath *et al.*, 2005].

[12] Version 3.0 of the ACE-FTS retrieval software, similar to the previous v2.2 [Boone *et al.*, 2005], was used for the HFC-23 VMR retrievals. In short, vertical VMR profiles of trace gases (along with temperature and pressure) are derived from the recorded transmittance spectra via a non-linear least squares global fit to the selected spectral region(s) for all measurements within the altitude range of interest. HFC-23 retrievals were performed over the altitude range 10 km to 25 km using a microwindow centered at 1150 cm^{-1} with a width of 20 cm^{-1} . Interferers in this region (retrieved simultaneously with HFC-23) were H_2O , H_2^{18}O , HDO , O_3 , $^{18}\text{O}^{16}\text{O}^{16}\text{O}$, $^{16}\text{O}^{18}\text{O}^{16}\text{O}$, N_2O , $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}^{14}\text{N}^{18}\text{O}$, $^{14}\text{N}^{14}\text{N}^{17}\text{O}$, CH_4 , $^{13}\text{CH}_4$, CH_3D , CFC-12 (CCl_2F_2), and HCFC-22 (CHF_2Cl). Atmospheric pressure and temperature profiles and the tangent heights of the measurements were taken from v3.0 processing of the

ACE-FTS data. Absorption cross sections for CFC-12 and HCFC-22, plus the spectroscopic line parameters for all molecules except HFC-23 were taken from the HITRAN 2004 database [Rothman *et al.*, 2005]. For HFC-23, a set of pseudolines covering 1100 to 1240 cm^{-1} derived from spectra recorded by Chung [2005] were used, as previously described in section 2.

[13] The transmittance spectrum for a single ACE measurement from occultation ss11950 (recorded on 31 October 2005 over Nunavut, a territory of northern Canada) at a tangent height of 10.4 km is given in Figure 1 (top). The most saturated lines in this spectrum are due to absorption of N_2O , with large contributions arising from absorption of O_3 , CH_4 and H_2O . Figure 1 (middle) reveals the observed – calculated residuals for the retrieval. Figure 1 (bottom) gives the HFC-23 contribution to the measured ACE spectrum; overlaid on this is the calculated contribution of HFC-23 absorption for this measurement (about 4%).

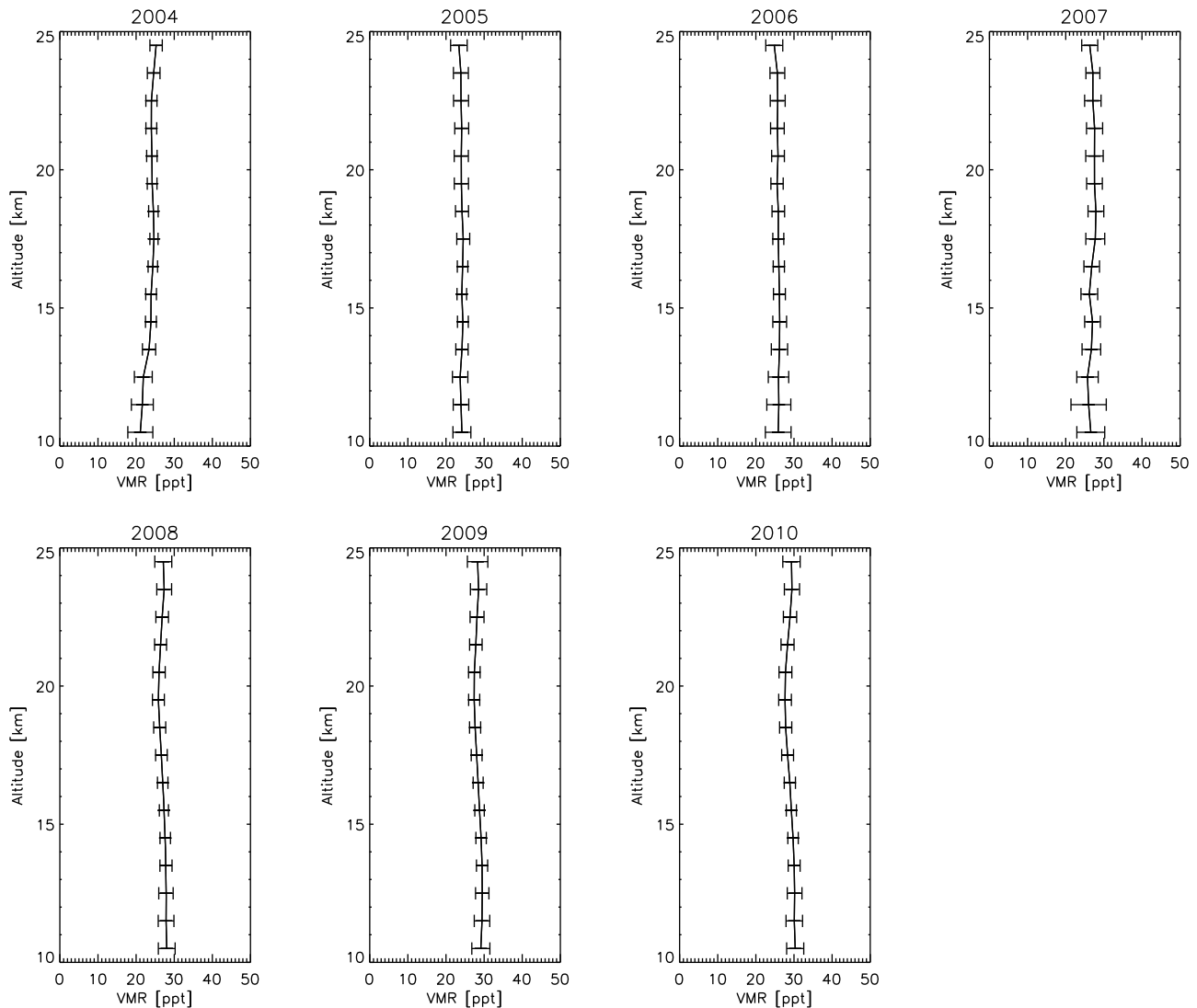


Figure 2. Median global ACE HFC-23 profiles, plotted from 10.5 to 24.5 km, for the years 2004–2010. Errors at each altitude are taken as one median absolute deviation of the VMR distribution for that year.

[14] In total, 8809 ACE occultations recorded between 2004 and 2010 were processed. Median global profiles were produced by filtering the retrievals by year. These median profiles, plotted from 10.5 to 24.5 km, are shown in Figure 2, and comprise 314, 825, 645, 149, 1807, 2258, and 2811 occultations, respectively, for each year from 2004 to 2010. Errors at each altitude are taken as one median absolute deviation (MAD) of the VMR distribution for that year. (For a data set, the MAD is defined as the median of the absolute deviations from the data's median. It measures the spread of values within a data set but with outliers given less weighting than when calculating the standard deviation.) Since HFC-23 has a long total atmospheric lifetime of 222 years [Montzka *et al.*, 2011] compared with typical transport times, one expects reasonably constant VMR profiles with altitude, as observed in Figure 2.

3.2. MkIV Interferometer

[15] The JPL MkIV interferometer [Toon, 1991; Toon *et al.*, 1999] is a balloon-borne FTS that records solar

occultation spectra in the 650–5650 cm^{-1} spectral range at a resolution of 0.01 cm^{-1} . There have been 21 flights between 1989 and 2007, principally over Fort Sumner, New Mexico, with some over Esrange, Sweden, and Fairbanks, Alaska. Several of these flights included both sunset and sunrise occultations. Data are presented for 24 occultations, of which seven were taken at high latitude (1997–2003). The MkIV retrievals use the same HFC-23 pseudoline list as for the ACE retrievals and typically cover the vertical range 10–40 km. For this work, the MkIV microwindows and interfering gases were chosen to be identical with those used by ACE, to minimize unnecessary differences.

4. Trends and Comparisons With Ground Measurements

[16] The ACE trend in the HFC-23 VMR over the time period 2004–2010 was derived by focusing only on tropical/subtropical observations. Owing to the natural uplift of air in the tropics, such an approach minimizes age-of-air effects

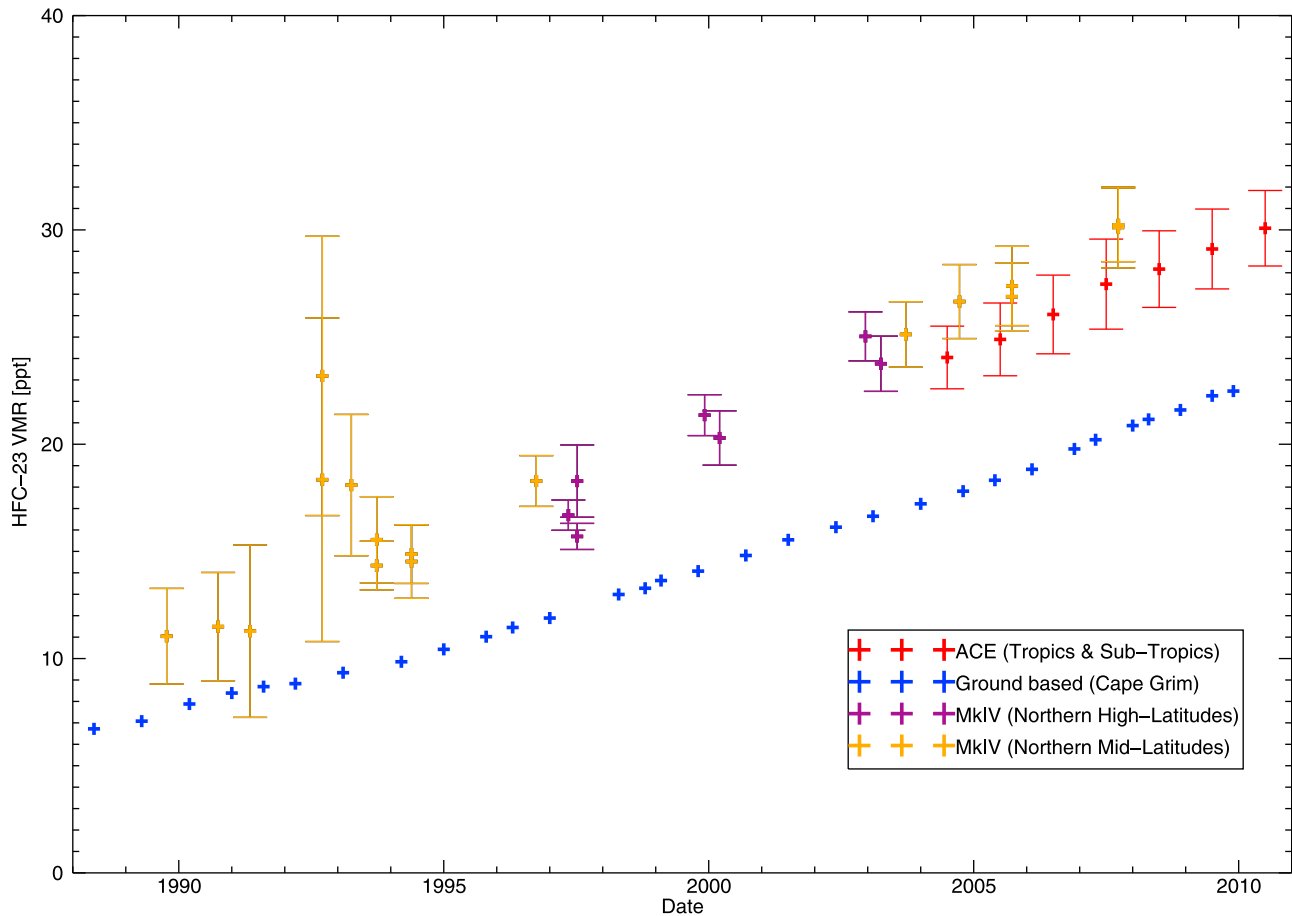


Figure 3. Trends in the growth of atmospheric HFC-23 using data from the ACE-FTS (2004–2010, tropical/subtropical data), the MkIV interferometer (1989–2007, midlatitude and high-latitude Northern Hemisphere data), and CGAA samples (1988–2009, ground-based data).

that can be present for higher-latitude measurements, and allows more appropriate comparisons with ground-based measurements. ACE median profiles over the latitude band 40°S to 40°N were produced, comprising 277, 476, 316, 128, 328, 432, and 314 occultations, respectively, for each of the 7 years. For each median profile, the VMRs over the altitude range 10 to 25 km were averaged to provide the annual value. These are plotted in Figure 3, with errors taken as one MAD of the VMRs used in each average. The distributions of the HFC-23 VMRs for each year are not strictly random (Gaussian) because of systematic errors and geophysical variations that add to the variability. Also, each plotted ACE value is an average over an individual year, throughout which the amount of HFC-23 in the atmosphere is slowly increasing with time.

[17] MkIV trends, derived from retrievals from 24 occultations, are presented in Figure 3. The plotted value for each profile is a weighted average of VMRs over the 10–25 km altitude range; errors bars are taken as the standard errors of the mean VMRs. Note the large error bars associated with the September 1992 MkIV balloon flight, which was adversely affected by aerosol from the 1991 Pinatubo eruption, preventing any limb spectra being measured below 22/23 km altitude.

[18] The MkIV VMRs show more scatter than the ACE values owing to the fewer occultations available (typically one per year). The last five (all midlatitude) MkIV occultations overlap with the time period of the ACE measurements. Since the MkIV observations are essentially snapshots in time at $\sim 34^\circ\text{N}$, whereas the ACE values in Figure 3 represent an annual average over a considerable portion of the globe, it is not expected that results from the two instruments will agree exactly.

[19] Comparisons are made with a representative selection of ground-based data as given by *Miller et al.* [2010] (Figure 3). These are HFC-23 measurements of Cape Grim air archive (CGAA) samples by two nearly identical AGAGE instruments (Medusa3 and Medusa9). As shown in Figure 3, the MkIV and ACE measurements are consistently $\sim 30\%$ higher than the Cape Grim measurements. Note that these ground measurements are expressed by *Miller et al.* [2010] as dry-gas mole fractions (in pmol mol^{-1}). These can be directly compared with the MkIV and ACE VMRs (in parts per trillion, ppt), for which the atmospheric contribution of water vapor is negligibly small at the retrieval altitudes. Since the bias between the remote sensing and ground measurements of HFC-23 appears to be multiplicative, growth rates are calculated as percentages rather than in terms of absolute

VMRs. Weighted nonlinear least squares fits of the relevant data to an exponential function of the form $a_1 \exp(a_2 t)$ were performed (t is the time in years); the growth rate is expressed as a percentage by $100[\exp(a_2) - 1]$. Using this approach, the ACE data show a growth of $3.9 \pm 1.2\%$ per year over the period 2004–2010, whereas the MkIV data exhibit a growth of $5.8 \pm 0.3\%$ per year over the period 1989–2007. If data for the seven high-latitude (65°N – 70°N) MkIV occultations (1997–2003) are omitted from the fit (i.e., only midlatitude (32°N – 37°N) data are used), the MkIV growth rate drops slightly to $5.3 \pm 0.4\%$ per year.

[20] Although surface sites can show nonlinear changes in emission rates, and the VMRs are not strictly expected to exhibit exponential behavior as a function of time, it was found that the Cape Grim data could be represented very well by an exponential function over the time periods of the ACE/MkIV measurements. In general, the trends in HFC-23 measurements are in good agreement. Since the CGAA data given by *Miller et al.* [2010] are only available until the end of 2009, a comparison is best performed by calculating an ACE trend over the period 2004 to 2009. Over this period, the surface data indicate an average growth of $4.7 \pm 0.3\%$ per year, slightly higher than the ACE value of $4.0 \pm 1.6\%$ per year.

[21] Over the period 1989–2007, the CGAA surface data indicate an average growth of $5.7 \pm 0.1\%$ per year, which compares well with the MkIV value of $5.8 \pm 0.3\%$ per year (and the midlatitude value of $5.3 \pm 0.4\%$). Since this is a comparison between northern midlatitude MkIV data and Cape Grim data (41°S), it is necessary to investigate whether there is a hemispheric difference in the surface growth rates of HFC-23. The study by *Miller et al.* [2010] includes in situ measurements from background sites in both the Southern and Northern Hemispheres, revealing higher concentrations in the north, where the main sources are located. For example, as shown in Figure 1 of *Miller et al.* [2010], AGAGE Medusa GC/MSD HFC-23 in situ measurements at Mace Head, Ireland, taken between October 2007 and December 2009, are consistently ~ 1 ppt higher than those at Cape Grim. Modeling results in Figure 1 of *Miller et al.* [2010] reveal consistently higher values in the Northern Hemisphere (30°N – 90°N) since 1978. These modeling results have been extracted, and the data for the period 1990–2007 fitted to an exponential function, giving a growth rate of $5.5 \pm 0.1\%$ per year. This is slightly lower than the value of $5.7 \pm 0.1\%$ per year determined from the CGAA data. This small difference of 0.2% is less than the error in the MkIV growth rate.

[22] As discussed by *Miller et al.* [2010], HFC-23 measurements of CGAA samples by two different AGAGE instruments are in excellent agreement despite the use of different instruments, different reference gases and a 1–3 years time span between analyses. Additionally, HFC-23 abundances determined from analyses of CGAA subsamples (spanning 1978–1997) at the University of East Anglia [*Oram et al.*, 1998] show excellent agreement with these AGAGE sample analyses despite the use of different instruments, independent calibration scales and a difference of 10 years between analyses dates. This high level of agreement suggests that the bias between ACE/MkIV and

ground-based measurements is primarily due to problems with the remote sensing data.

[23] In order to determine the origin of this bias, first one needs to consider the relative locations of the measurements as well as age-of-air effects. As explained earlier, surface HFC-23 measurements in the Northern Hemisphere are typically ~ 1 ppt higher than those in the Southern Hemisphere. However, the remote sensing data used in the trends are taken over the 10–25 km altitude range. This has various implications on the measured VMRs owing to the time it takes for air to pass from the troposphere to the stratosphere. For example, in the midlatitude lower stratosphere, the air is 2–3 years old. This is a slightly bigger effect than the interhemispheric gradient, and would tend to make the remote sensing measurements slightly smaller than the ground measurements. Clearly, this does not explain the observed bias. The most likely sources of error are discussed in section 5.

5. Spectroscopic Sources of Error in the ACE/MkIV Retrievals

[24] For a single ACE profile, the random statistical fitting errors in the HFC-23 VMRs are about 10%–15% with systematic errors on the order of 20%–25%. For the filtered median profiles, the random errors are small and the systematic errors dominate. For a single MkIV profile, the random errors are similar in magnitude to those for ACE. With only 24 occultations, it is difficult to assess the exact contribution of systematic errors to the MkIV retrievals, but they are likely similar in magnitude to those of ACE since both instruments use the same microwindow and spectroscopy. A number of spectroscopy-related contributions to the retrieval errors have been identified; these are outlined in sections 5.1–5.4. Subsequent processing versions of the HFC-23 retrieval software will need various improvements; for example, new laboratory HFC-23 spectra are required.

5.1. HFC-23

[25] It is most likely that the largest contribution to the systematic errors in the ACE/MkIV retrievals arises from the Chung HFC-23 laboratory spectra; the procedure used to generate the pseudolines has only a minor contribution. Despite the integrated band intensities agreeing well with the PNNL spectra to within 0.5%, this does not guarantee the quality of the original Chung spectra. Inconsistencies in the tabulated HFC-23 partial pressures have already been noted, possibly resulting from instabilities in the temperature or a leak in the sample cell. Thermometry problems at cold temperatures would also lead to systematic retrieval errors. Furthermore, the lowest temperature in the data set (214 K) is slightly higher than the lowest temperatures found in the UTLS, requiring extrapolation when performing retrievals; errors in these spectra will make this extrapolation less reliable. It also should be noted that the wave number range of the Chung measurements does not extend far enough to be confident of the true position of the spectral baseline. Errors in the baseline will result in systematic errors in the spectra once the band intensities have been adjusted to agree with the PNNL spectra. The exact contribution of HFC-23 spectroscopy to the retrieval error is difficult to quantify, but it is unlikely to account for the entire bias. In

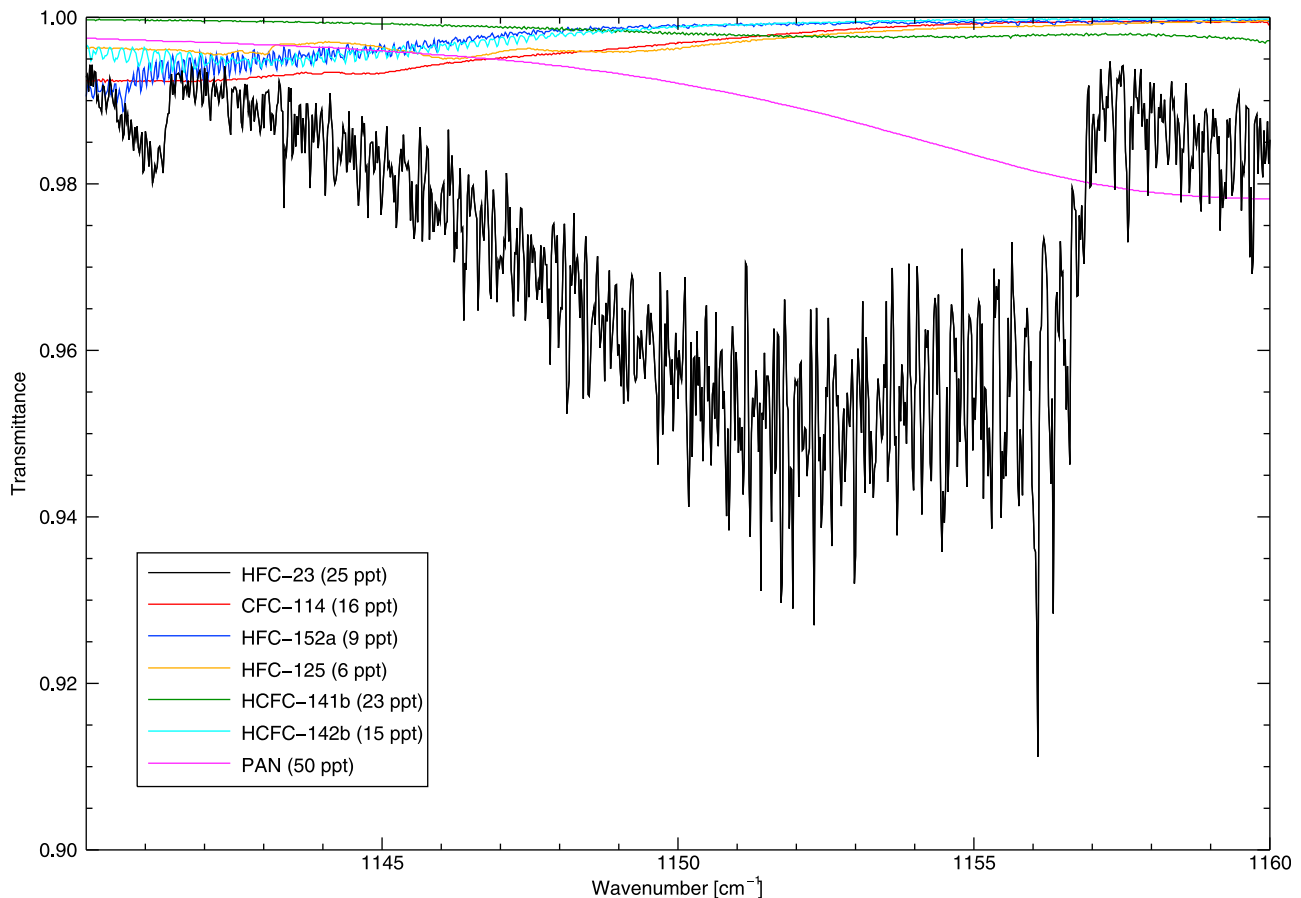


Figure 4. Approximate calculated transmittance contributions to the microwindow for HFC-23 (25 ppt), HCFC-141b (23 ppt), HCFC-142b (15 ppt), CFC-114 (16 ppt), HFC-125 (6 ppt), HFC-152a (9 ppt), and PAN (50 ppt). These molecules contribute weakly to the spectrum but were not included in the ACE/MkIV retrievals.

order to more accurately quantify the amount of HFC-23 in the atmosphere using infrared remote sensing techniques, new and improved HFC-23 laboratory spectra are required.

5.2. Weak, Broad Absorbers

[26] Several absorbers with broad spectral features contribute weakly to the spectrum microwindow but were not included in the ACE/MkIV retrievals. These are HCFC-141b, HCFC-142b, CFC-114, HFC-125, HFC-152a, and $\text{CH}_3\text{COO}_2\text{NO}_2$ (peroxyacetyl nitrate; PAN). Figure 4 gives approximate calculated transmittance contributions to the microwindow for HFC-23 and these molecules. Note that CFC-114, HFC-125 and HFC-152a have never previously been retrieved from ACE-FTS spectra. The contributions for these molecules were determined using cross sections from the HITRAN database, and ground measurements for their abundances [Montzka *et al.*, 2011; Advanced Global Atmospheric Gases Experiment, 2011, <http://agage.eas.gatech.edu/>]. Both HCFC-141b and HCFC-142b are retrieved in ACE v3.0 processing. HCFC-141b has a similar spectral shape to HFC-23, and has the most potential for causing problems with the HFC-23 retrieval, however the contribution is too small to introduce significant errors. Since the

HCFC-141b atmospheric concentration is increasing rapidly [Brown *et al.*, 2011], subsequent ACE processing for HFC-23 will adjust the microwindow to include a strong Q-branch for HCFC-141b and include the molecule as an interferer. HCFC-142b is also too small to produce significant errors in HFC-23 retrievals.

[27] Tests were performed on MkIV retrievals in order to assess the impact of including HCFC-141b and HCFC-142b as interferers in the microwindow. The inclusion of these species and a widening of the microwindow (centered at 1155.0 cm^{-1} with a width of 37.2 cm^{-1}) cause only small changes in the MkIV HFC-23 VMRs, which are within the random statistical fitting errors. Therefore, not including these species as interferers in the microwindow makes no noticeable contribution to the observed bias for the MkIV occultations. It is expected that this also holds true for ACE retrievals because the forward models for both retrieval schemes use the same spectroscopy.

[28] CFC-114, HFC-125, and HFC-152a all have weak spectral features (~ 0.5 to 1% absorption at the lowest altitudes) within the fitting window, but these features are not well aligned with the HFC-23 spectral feature and will therefore not introduce large errors in the retrievals.

However, the rapidly increasing atmospheric concentrations of HFC-125 and HFC-152a may necessitate their inclusion in future processing versions.

[29] PAN has a slightly larger contribution to ACE spectra than the other five molecules. Tests in which PAN was included as an interferer in ACE retrievals yielded very little change in the HFC-23 profile, typically a fraction of a percent at all altitudes. As seen in Figure 4, the contribution of PAN to the fitting window is approximately linear with spectral frequency, so much of its effect is absorbed into the fitted baseline parameters and does not have a major impact on the retrieval. Note that Figure 4 assumes a VMR of 50 ppt, but in reality, PAN has a variable atmospheric abundance [Glatthor *et al.*, 2007; Moore and Remedios, 2010], with background levels below this value above 15 km (i.e., the contribution in Figure 4 is overestimated). PAN can be enhanced in biomass burning plumes above typical background values [Coheur *et al.*, 2007], so ACE occultations that sample these plumes could suffer from increased error in the HFC-23 retrievals. Subsequent ACE processing will include PAN as an interferer.

5.3. O₃

[30] The HFC-23 microwindow also includes contributions from a large number of relatively strong O₃ lines, including far-wing contributions from O₃ lines outside the fitting window; the associated residuals are typically larger than the noise. Forward model calculations for the ACE-FTS typically include contributions from all lines within 0.5 cm⁻¹ of the fitting window; that is, the extent of the instrumental line shape (ILS) is ± 0.5 cm⁻¹. Tests were performed on a selection of ACE occultations, in which the calculation range was extended to 4.8 cm⁻¹, the maximum capability of the software. This significantly improves the residuals associated with the relatively strong (but not overly saturated) O₃ lines (i.e., the retrieved HFC-23 VMR profiles become less noisy), although it generally does not reduce the residuals to the noise level, nor does it improve the systematic bias at all. It is possible that the ILS needs to be extended even further, however since there is little change to the residuals when the ILS is extended from 3.6 to 4.8 cm⁻¹, it is possible that these remaining residuals arise from missing O₃ hot bands or neglected O₃ line mixing. If so, this would introduce a systematic bias in the retrieved HFC-23 VMRs. It is difficult to estimate the magnitude of this bias without a more detailed knowledge of the limitations in the O₃ spectroscopy, however it is likely to be small.

5.4. Additional Contributions

[31] ACE and MkIV often suffer from bad residuals for H₂O lines, particularly for ACE tropical occultations where H₂O VMR is elevated. Tests were performed on a selection of ACE occultations by excluding spectral points in the vicinity of strong H₂O lines, that is, giving them zero weight in the least squares fit. The resulting retrieved HFC-23 VMR profiles become slightly less noisy (i.e., the random statistical fitting errors are reduced), however there is no improvement in the systematic bias at all.

[32] The microwindow contains CH₃D Q branches which are near coincident with a sharp gradient in the HFC-23 spectrum (1156–1157 cm⁻¹). However, there are currently

no line-mixing parameters available for these Q branches that could be used to reduce residuals from neglected line mixing.

6. Conclusions

[33] For the first time, HFC-23 has been detected in the atmosphere from remote sensing measurements taken by two solar occultation instruments: the ACE-FTS and the MkIV balloon interferometer. ACE data (40°S to 40°N) reveal a 2004–2009 trend of $4.0 \pm 1.6\%$ per year (or $3.9 \pm 1.3\%$ per year for 2004–2010) in the growth of HFC-23, slightly lower than the surface observations from CGAA samples over the same time period ($4.7 \pm 0.3\%$ per year). The midlatitude and high-latitude MkIV data (1989–2007) indicate a growth rate of $5.8 \pm 0.3\%$ per year ($5.3 \pm 0.4\%$ per year for just the midlatitude data), similar to the Cape Grim surface trend of $5.7 \pm 0.1\%$ per year over the same period. The absolute HFC-23 VMRs measured by ACE and MkIV in the UTLS are in good agreement with each other, but are ~30% larger than the ground-based measurements. This bias is most likely caused by spectroscopic errors in the forward model.

[34] Although not as precise as measurements provided by ground-based networks, remote sensing measurements, in particular those by the ACE-FTS instrument, are capable of probing long-lived trace constituents through different parts of the Earth's atmosphere. Such measurements are particularly important in determining the GWPs of greenhouse gas molecules; global distributions of these gases, especially their vertical profiles, are needed to accurately determine radiative forcings and atmospheric lifetimes. Before this can be achieved for HFC-23, however, some more laboratory spectroscopic work and improvements in the retrieval are required. Most importantly, new measurements of HFC-23/synthetic-air absorption spectra over a range of atmospherically relevant temperatures and pressures are required.

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