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Spectroscopic detection of COClF in the tropical and mid-latitude lower stratosphere

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Abstract

We report retrievals of COClF (carbonyl chlorofluoride) based on atmospheric chemistry experiment (ACE) solar occultation spectra recorded at tropical and mid-latitudes during 2004–2005. The COClF molecule is a temporary reservoir of both chlorine and fluorine and has not been measured previously by remote sensing. A maximum COClF mixing ratio of 99.7 ± 48.0 pptv (10^{-12} per unit volume, 1 sigma) is measured at 28 km for tropical and subtropical occultations (latitudes below 20° in both hemispheres) with lower mixing ratios at both higher and lower altitudes. Northern hemisphere mid-latitude mixing ratios (30–50°N) resulted in an average profile with a peak mixing ratio of 51.7 ± 32.1 pptv, 1 sigma, at 27 km, also decreasing above and below that altitude. We compare the measured average profiles with the one reported set of in situ lower stratospheric mid-latitude measurements from 1986 and 1987, a previous two-dimensional (2-D) model calculation for 1987 and 1993, and a 2-D-model prediction for 2004. The measured average tropical profile is in close agreement with the model prediction; the northern mid-latitude profile is also consistent, although the peak in the measured profile occurs at a higher altitude (2.5–4.5 km offset) than in the model prediction. Seasonal average 2-D-model predictions of the COClF stratospheric distribution for 2004 are also reported.

Keywords: Remote sensing; Stratospheric chemistry; Infrared atmospheric remote sounding; Measurement–model comparisons; Stratospheric chlorine chemistry; Stratospheric fluorine chemistry

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1. Introduction

There now exists evidence from ground-based solar absorption spectra, model calculations, and solar occultation measurements that chlorine loading is near its maximum in the lower stratosphere and it is expected to slowly decline with time [1–4]. However, because of the crucial role of chlorine in ozone loss and possible climate-induced changes in atmospheric chemistry [5], there remains a need to monitor stratospheric chlorine and improve methods for quantification of chlorine and fluorine chemistry from both ground-based and space-based observations. Infrared measurements covering nearly all components of the chlorine and fluorine budgets (with a few exceptions) can be retrieved directly from high-resolution solar occultation spectra [6–10], and hence such observations are needed for verification of model chemistry and for prediction of future trends.

One halogen-bearing molecule not yet derived from infrared remote sensing measurements is COClF. Carbonyl chlorofluoride or chlorofluorocarbonyl (COClF), also referred to as CFClO or OCClF, is a reservoir species that results from the breakdown of CCl_3F [6–13]. It is the most easily photolyzed F-containing breakdown product with a mixing ratio that decreases rapidly above the peak. Modeled COClF assuming a 3% per year increase between 1990 and 1994 was used to estimate stratospheric chlorine from Atmospheric Trace MOlecule Spectroscopy (ATMOS) measurements at northern mid-latitudes (35–49°N) and the northern subtropics during 1994 [13]. Production of COClF is analogous to the CH_4 oxidation scheme, and is based on the assumption that in chlorofluorocarbons (CFCs), all C–Cl bonds break before C–F bonds and for HCFCs, C–H bonds break first, followed by C–Cl bonds, and then C–F bonds. This implies that CCl_2F_2 will breakdown to form COF_2 and that CCl_3F will breakdown to form COClF as follows:

$$CCl_3F + h\nu \rightarrow CCl_2F + Cl, \quad (1)$$

$$CCl_2F + O_2 + M \rightarrow CCl_2FO_2 + M, \quad (2)$$

$$CCl_2FO_2 + NO \rightarrow COClF + Cl + NO_2, \quad (3)$$

$$COClF + h\nu \rightarrow Cl + COF. \quad (4)$$

Removal of COClF by $O(^1D)$ was also accounted for with the modeled COClF distribution reported as a function of latitude and different seasons in 1989 [13].

The global distribution of COClF [13] for 1989 was predicted to be relatively symmetric about the equator with the highest VMR of ~100 pptv (1 pptv = 10^{-12} per unit volume) at 20 hPa. The model distribution showed lower maximum VMRs with peaks shifted to higher pressure levels in both hemispheres for March and June 1989. Photolysis causes the reduction at higher altitudes with only a very small COClF seasonal variation predicted. Both chlorine and fluorine atoms are contained in COClF with loadings that have changed with time, but to our knowledge, no recent model COClF predictions or measurements of COClF loadings have been reported.

The purpose of this paper is to describe the analysis of infrared solar occultation spectra recorded by the atmospheric chemistry experiment (ACE) Fourier transform spectrometer (FTS) [14] for COClF concentrations in the lower stratosphere. Absorption by COClF is very weak even in the high-resolution ACE spectra, so we report averages of retrievals from spectra recorded during 2004 and 2005 at tropical–subtropical (20°S–20°N) and northern mid-latitudes (30–50°N). The retrieved profiles for both latitude bands are plotted against two-dimensional (2-D) model calculations for the same time period and are compared with previous model predictions, the single reported measurement set obtained during northern mid-latitude aircraft flights sampling the upper troposphere and lower stratosphere in 1986 and 1987 [15], and model predictions for the ACE measurement time period.

2. Measurements

The ACE payload, also known as SCISAT-1, was successfully launched on 12 August 2003 into a 74° inclined orbit by a NASA-supplied Pegasus XL at 650 km altitude [13]. This small Canadian-designed and built satellite contains three instruments with a shared field of view, and with the primary goal of recording

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high-resolution atmospheric spectra taking advantage of the high precision of the solar occultation technique. The infrared instrument is an FTS that records solar spectra below altitudes of 150 km at a spectral resolution of 0.02 cm^{-1} (maximum optical path difference of ±25 cm) with a 1.25 mrad diameter field of view. The spectral cover 750–4400 cm^{-1} and are analyzed unapodized to take full advantage of the high spectral resolution. The instrument is self-calibrating as low Sun solar occultation spectra are divided by exoatmospheric spectra from the same occultation. The ACE orbit yields tropical to high-latitude occultations in both hemispheres with a 3–4 km vertical resolution. Additional instruments onboard SCISAT-1 are measurement of aerosol extinction in the stratosphere and troposphere by occultation (MAESTRO), a two channel UV-visible spectrophotometer, and two imagers with optical filters at 0.525 and 1.02 μm to provide extinction from analysis of solar disk images.

3. Analysis and comparison with model predictions

Very limited information has been reported on the infrared spectrum of COClF. A spectrum of the strong infrared COClF ν_1 fundamental band at 1876 cm^{-1} covering 1790–1910 cm^{-1} recorded at 0.02 cm^{-1} resolution was reported in an atlas of infrared laboratory spectra [16]. The atlas spectrum shows a series of prominent P-branch features at 1860–1870 cm^{-1}, a Q branch at 1875.8 cm^{-1}, and R-branch transitions extending to 1890 cm^{-1}. Our study focuses on ACE solar occultation measurements obtained in the tropical–subtropical region and at northern mid-latitudes during 2004 and 2005. We base our analysis on COClF line parameters from the ATMOS supplemental list [17,18]. That list covers two regions with parameters for the ν_1 band extending from 1850.078 to 1907.929 cm^{-1}. Those parameters were added in the 1995 compilation [18]. Line intensities are described as very crude with a reported uncertainty of a factor of 3. All lines have a lower state energy of 345.0 cm^{-1}, and an air-broadening coefficient of 0.1 cm^{-1} atm^{-1} at 296 K with $T^{-0.75}$ assumed for the coefficient of the temperature dependence of the air-broadening coefficient, where T is the temperature. The laboratory spectra were measured at room temperature at high spectral resolution. More recently, an analysis of the 6 fundamental bands of the $CO^{35}ClF$ isotopologue was reported based on spectra of both ^{35}Cl-enriched and natural samples recorded between 340 and 2000 cm^{-1} at better than 0.0033 cm^{-1} spectral resolution [19]. Although the analysis did show the comparison of a measured and a simulated spectrum in selected regions of the ν_1 band, no intensity measurements were reported, and no linelist based on this work appears in public databases such as the HITRAN 2004 compilation [20]. We also were unable to find any other studies reporting intensities, and were unsuccessful in locating air-broadening coefficients or pressure-induced line shift coefficients for individual air-broadened lines of the ν_1 band.

The spectral fitting algorithm used in the present analysis retrieves simultaneous profiles for COClF and interferences of all measurements over a pre-specified altitude range [21–23]. The retrieval approach is similar to the one adopted by ACE [24] and the method of Carlotti [25]. It is based on nonlinear least squares fitting of spectra for the target molecule and interfering molecules. Our analysis combines the COClF lines from the 1995 ATMOS supplemental linelist [18], the ACE solar spectra, and spectral parameters for other molecules from HITRAN 2004 [20] with the retrieved profiles of temperature, pressure, and tangent altitude for individual ACE occultations [24]. A refractive ray tracing program was used with the ACE-derived temperature profile and tangent heights to calculate airmass-weighted pressures, temperatures, and atmospheric ray paths for individual ACE occultations. The calculation of the COClF rotational and vibration partition function [23] assumes vibrational band locations in close approximation to those reported in the more recent study [19].

Similar to other infrared experiments (e.g., [9,22,24,26–28]), a set of microwindows were selected for analysis. The 8 selected windows are reported in Table 1 with the interferences fitted in addition to COClF in the retrievals. The list includes the Q branch at 1875.8 cm^{-1}, though similar to predicted absorption COClF in the other windows, it is near the noise level, even in the tropical lower stratosphere. The full set of target and interfering species was used to retrieve each occultation profile.

As the absorption by COClF is very weak, several empirically selected parameters were used to exclude occultations with noisy measurements at one or more altitudes. A parameter was fitted to model the effective resolution to account for additional self-apodization that decreases the effective resolution of the instrument

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Table 1
Selected microwindows

Minimum (cm^{-1})	Maximum (cm^{-1})
1860.00	1860.70
1861.90	1863.20
1864.00	1864.60
1864.90	1866.00
1866.60	1867.00
1868.50	1869.10
1870.40	1870.75
1874.50	1875.40

Interferences fitted in the analysis were H_2O, CO_2, O_3, N_2O, and NO for all regions. Maximum altitude was set to 30 km for both tropical and mid-latitude occultations. Tropical occultations were fit with the minimum altitude set to 19 km and 17 km was selected as the minimum for mid-latitude occultations.

as a function of wavenumber [24]. Profiles containing mixing ratios with large uncertainties relative to the measured value were also discarded from the tropical measurement set.

Fig. 1 presents normalized measured and simulated solar spectra for a portion of the spectra range covered by ACE in the infrared. The interval was selected because it is near the maximum of the predicted absorption in the P branch of the v_1 COClF band, the strongest infrared band. A reference a priori COClF mixing ratio distribution was selected to provide a spectral depth for the stronger COClF spectral features similar to those measured in the average spectrum. The mean spectrum was obtained by averaging 655 spectra from 178 occultations with tangent heights between 20 and 26 km from measurements during 2004. Molecule-by-molecule simulations for COClF and the most significant interferences are shown below. The parameter to model the effective resolution to account for additional self-apodization was not included in the simulations. As a consequence, the simulated line shape is narrower than in the measured coadded spectrum with ringing noticeable for the stronger simulated lines. The measured and simulated spectra illustrate the complexity of the absorption in the region. Additionally, as strong solar CO lines occur in the COClF v_1 band region, it was necessary to avoid intervals containing strong solar CO lines in the exoatmospheric average spectrum because of minor imperfections in the cancelation of those features in the ratioed spectrum used in the retrievals. A similar procedure of ratioing low to exoatmspheric spectra was used previously in the analysis of ATMOS spectra solar occultation spectra [23].

Tropical measurements recorded during February, April, August, October, and December in 2004 and February and April 2005, and northern mid-latitude measurements from February, March, April, June, July, August, September, and December of 2004 and March, April, and May of 2005 were analyzed. Mean profiles were calculated for those two latitudinal regions with objective criteria used to exclude occultations based on the statistical uncertainty of the fit and a parameter to quantify the quality of the fit to the instrumental line shape. After exclusion of occultations with these objective criteria, 159 of the 321 tropical occultations were retained. Only data from 30 occultations of the available 337 at northern mid-latitudes were kept with similar criteria as applied for the tropical–subtropical occultations.

Fig. 2 presents two panel plots that show average spectra and residuals (measured minus calculated differences) derived from all ACE tropical spectra measurements in 2004 at latitudes between 20°S and 20°N and altitudes between 22 and 24 km. An average spectrum near 23 km was produced from 221 spectra. The selected spectral regions for the two intervals are located near the maximum of COClF absorption in the P branch. Residuals obtained assuming the mean retrieved profile and those obtained with the COClF mixing ratio set to zero at all altitudes are shown in the upper panel on an expanded scale. Asterisks mark the locations of significant differences corresponding to the locations of COClF absorption lines. Interfering molecules fitted in the analysis were H_2O, CO_2, O_3, N_2O, and NO assuming the temperature profile and tangent height at 24 km inferred by the ACE version 2.2 software [24]. Similar comparisons with other windows near the COClF absorption maximum also provide evidence for COClF absorption in the ACE tropical spectra.

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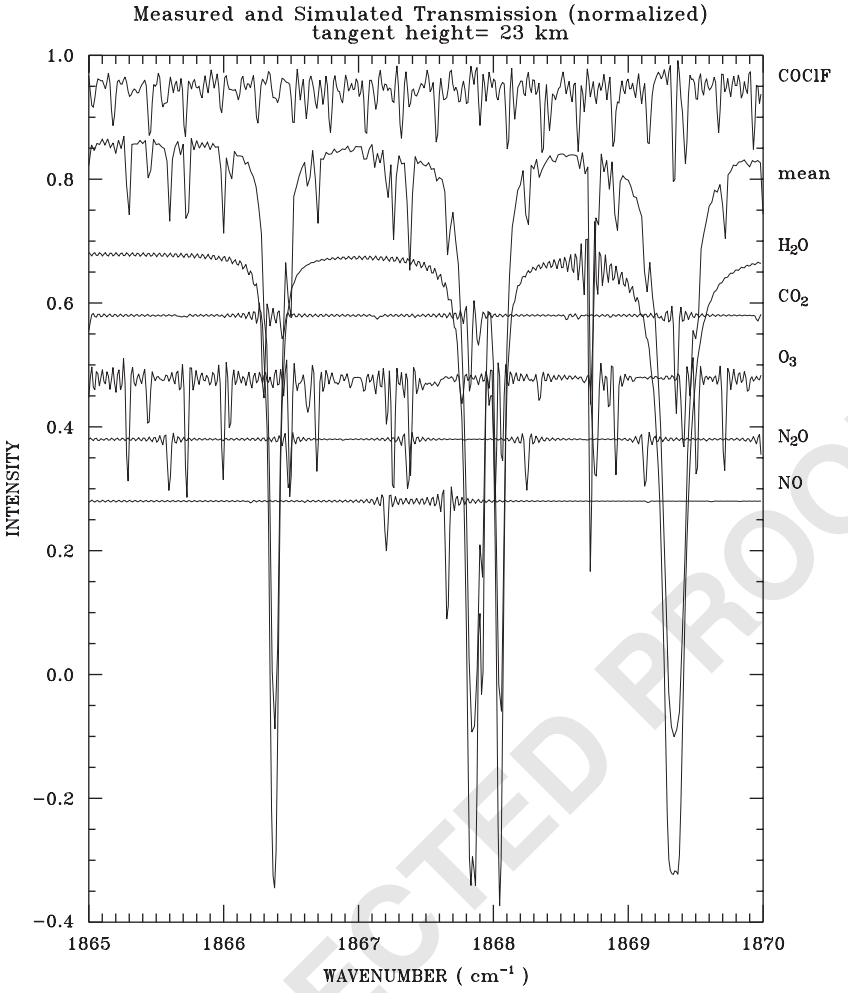

Fig. 1. Comparison of an average ACE tropical spectrum with molecule-by-molecule simulations for an altitude of 23 km. Spectra are normalized and offset vertically for clarity. As COClF is a weak absorber, a reference a priori mixing ratio profile has been scaled with a multiplicative factor to produce COClF spectral features with absorption depths similar to those in the measured tropical–subtropical average spectrum. The second spectrum is an average of 655 spectra from 178 occulations between latitudes of 20°S and 20°N and altitudes between 20 and 26 km during 2004.

The only reported lower stratospheric measurements of COClF were derived with the matrix isolation FTS technique [29] from measurements recorded during 5 aircraft flights in 1986 and 1987 between Germany and Spitzbergen (50–78°N) [14]. The mixing ratio of COClF was below the detection limit of 4 pptv at altitudes below the tropopause. A rapid increase of the COClF mixing ratios relative to the tropopause height was measured at higher altitudes increasing to 18 ± 5 pptv at 5 km above the tropopause.

As measurements of COClF are so limited and previous model studies were for 1989 [13] and September 1993 [10], model calculations appropriate for the ACE measurement time were performed with the Atmospheric and Environmental Research, Inc. (AER) 2-D chemical-transport model [30–34]. As described in those previous studies, the AER model domain extends from the ground to 60 km with a vertical resolution of approximately 1.2 km and from pole to pole with horizontal resolution of 9.5°. Model temperatures and transport/circulation are prescribed according to climatology and do not respond to changes in aerosols or chemical species. The model includes full O_x, HO_x, CHO_x, NO_x, ClO_x, and BrO_x photochemistry. Loss of COClF is by photolysis and reaction with $O(^1D)$ assuming JPL-2006 rates [35]. A surface boundary of 253.26 pptv for CCl_3F in 2004 was assumed. Production from CCl_3F total loss (photolysis and $O(^1D)$) assumes COClF is immediately produced when CCl_3F reacts. Washout is parameterized as a first-order loss

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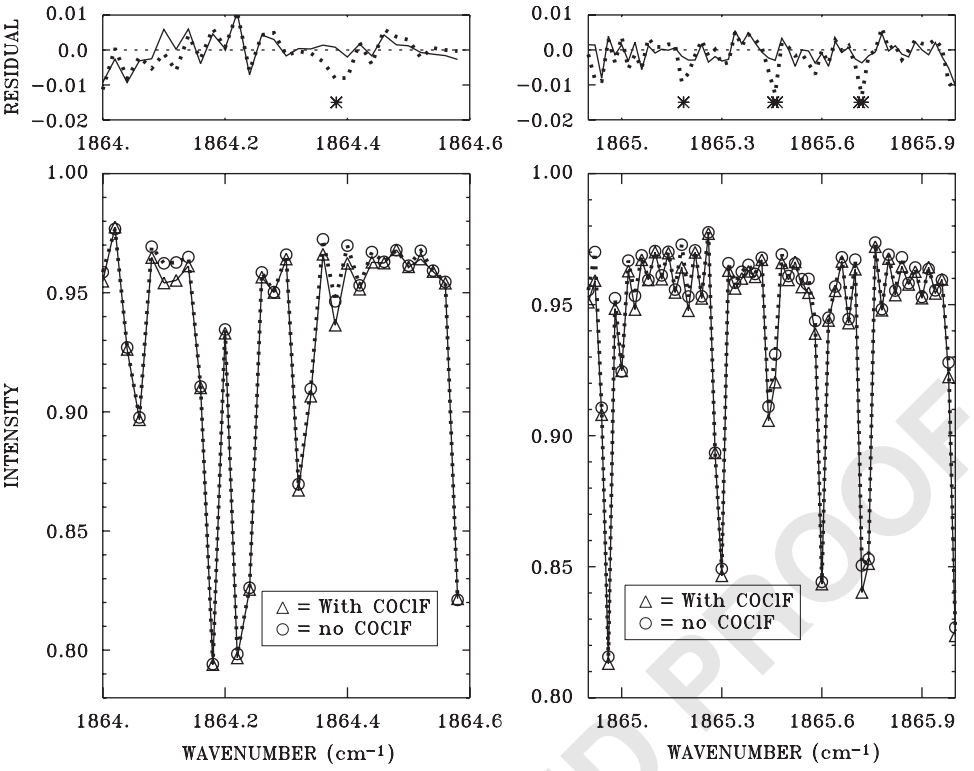

Fig. 2. Bottom panels: comparison of averages of all ACE tropical spectra measurements in 2004 at latitudes between 20°S and 20°N and altitudes between 22 and 24 km obtained with the best-fit COClF profile with those obtained assuming the COClF mixing ratio is zero at all altitudes. Upper panels: residuals (measured minus calculated signals) on an expanded vertical scale. Asterisks mark locations of stronger COClF features in the sample intervals.

rate below 10 km with a dependence on altitude as follows: 5 days for 0–2 km, 6.5 days at 2.9 km, 8 days at 4.0 km, 10 days at 5.2 km, 20 days at 6.4 km, 30 days at 7.6 km, and 40 days at 8.8–10 km. Tests run with the washout rate half or double of those values produce no changes in the stratosphere. A washout rate corresponding to a lifetime of 40 days up to the tropopause in the tropics made a 4% difference at 17 km and no difference above 20 km in the tropics.

Fig. 3 compares the ACE measurements for two latitude bands with the AER model predictions for 2004. The tropical measurements and model predictions both show an increase with altitude above 20 km with the measurements reaching a maximum mixing ratio of 99.7 ± 48.0 pptv (1 sigma) at 28 km, declining rapidly above, very similar to the prediction for 1989 [10]. Mid-latitude mixing ratios (30–50°N) resulted in a profile with lower mixing ratios at all altitudes and a maximum VMR of 51.7 ± 32.1 pptv, 1 sigma, at 27 km, consistent with the AER 2-D-model maximum although the model-predicted COClF mid-latitude peak is reached 3 km lower than that retrieved from the measurements. The AER model predictions for tropical and mid-latitudes also appear to be roughly consistent with those predicted for the 1989 northern mid-latitudes, but our measured mid-latitude maximum of 51.7 ± 32.1 pptv is lower than the model-predicted September 1993 maximum of 83 pptv at 26 km [13]. However, there is consistency when considering the large statistical uncertainty of our mean profile measurement. Profile measurements above 30 km likely underestimate the precision as window selection was based on interferences at 18–30 km (Table 1) with absorption weaker than those in the coadded spectra illustrated in Figs. 1 and 2. Lower mixing ratios and large uncertainty at northern mid-latitudes make comparison of our result with the one set of mid-latitude COClF lower stratospheric measurements obtained within 5 km of the tropopause in 1986 and 1987 [15] difficult. However, their failure to detect COClF mixing ratios in the troposphere above the measurement uncertainty of 4 pptv provides evidence

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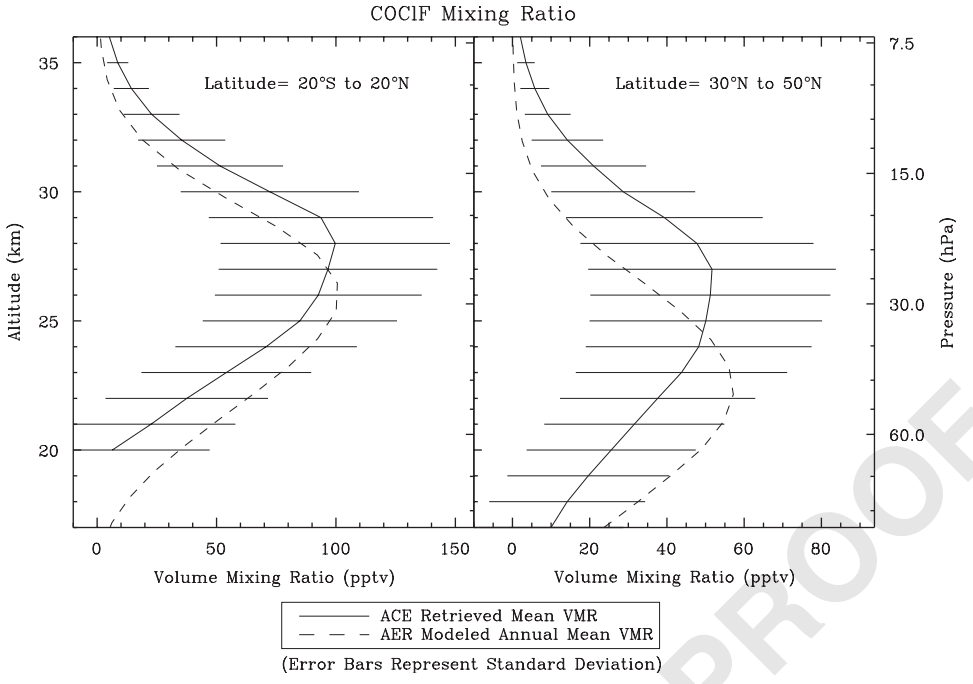

Fig. 3. Comparison of mean ACE COClF mixing ratios vs. altitude for tropical latitudes (20°S–20°N) and northern mid-latitudes (30–50°N) from 2004 and 2005 with AER two-dimensional model calculations for 2004 (annual average). Horizontal error bars indicate standard deviations. Approximate pressures are indicated on the right vertical axis.

for the importance of tropospheric washout in the upper troposphere and the need for its inclusion in model predictions.

Fig. 4 presents the AER 2-D-model COClF global distribution predicted as a function of season for 2004. The model shows a maximum in the tropical stratosphere with no significant seasonal variation, consistent with the higher tropical than mid-latitude maximum measured by ACE, the single set of 1986 and 1987 in situ measurements [15], and previously reported model predictions [10,13]. The AER global COClF distribution for 2004 is close to a prediction by one of us (R. Nassar) obtained by scaling and vertically shifting the 2-D-model prediction for 1989 [13]. Latitude–height COClF crosssections predicted for the month of December based on 1990 tropospheric source gas mixing ratios had a predicted peak mixing ratio of 0.11 ppbv in the tropical lower stratosphere [36] with tropospheric washout assumed, though details of the mechanism and pathway parameterization were not described.

4. Summary and conclusions

We have reported spectroscopic evidence for lower to middle stratospheric carbonyl chlorofluoride (COClF) from an analysis of ACE spectra at tropical–subtropical latitudes (20°S–20°N) and northern mid-latitudes (30–50°N) during 2004 and 2005. The results show mixing ratio profiles with maxima in the lower stratosphere for both latitude bands, consistent with AER 2-D-model calculations for 2004. Our results provide the first quantitative measurement of carbonyl chlorofluoride in the lower stratosphere. Our measured profiles are roughly consistent with predictions from similar models for 1989 [13] and September 1993 [10]. However, the uncertainties in our mean mid-latitude profile are too large to provide validation of the single reported set of northern hemisphere in situ measurements in the upper troposphere and lower stratosphere from 1986 and 1987 [15]. Although our analysis provides observational evidence for COClF in the lower stratosphere, laboratory studies are needed to obtain accurate intensities, air-broadening coefficients, and air-

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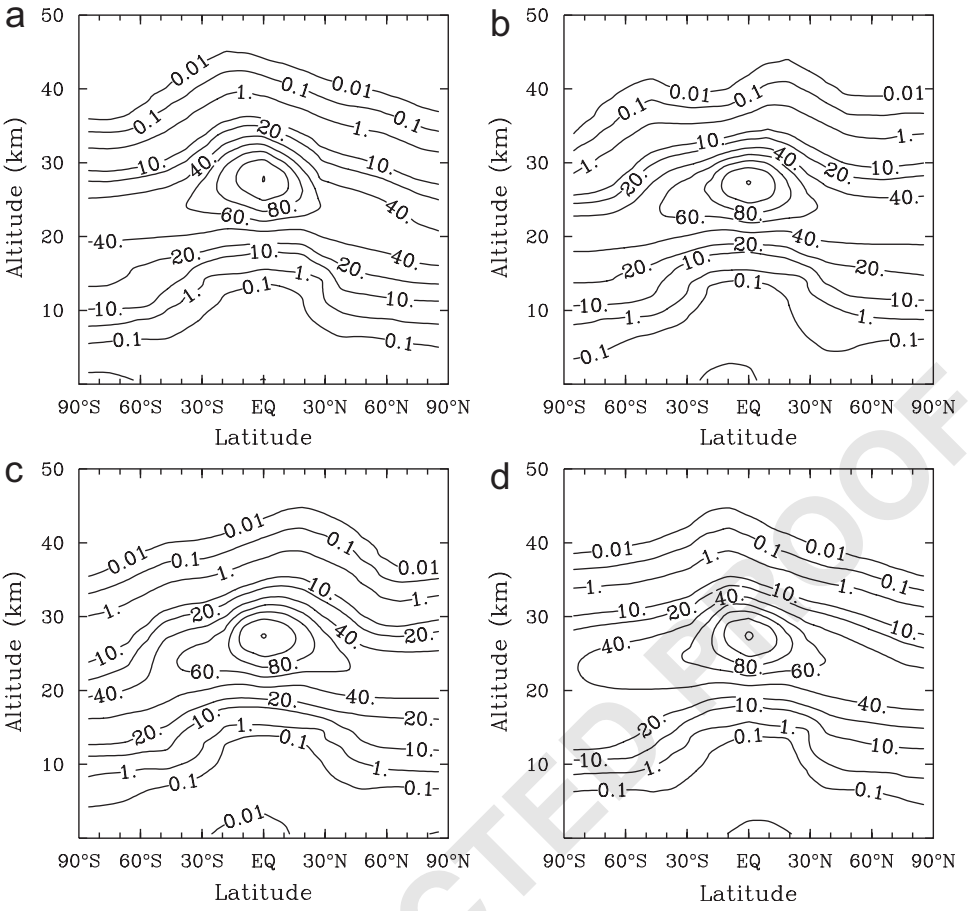

Fig. 4. COClF global distribution for 2004 predicted by the AER 2-D model for (a) March, (b) June, (c) September, and (d) December in units of pptv.

induced pressure shift coefficients for lower stratospheric temperatures to reduce the large uncertainty in our measured profiles due to the limited precision and accuracy of the assumed spectroscopic parameters. Results are needed for the v_1 band, the only one strong enough in the infrared for measurement over long atmospheric paths at high spectral resolution. Intensity measurements of the v_1 band are recommended as the highest priority for laboratory studies because of the factor of three uncertainty in the ATMOS value.

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