Total hydrogen budget of the equatorial upper stratosphere

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[1]   Water vapor and methane mixing ratios measured by the Halogen Occultation Experiment (HALOE), the Atmospheric Chemistry Experiment (ACE), and the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) along with simulations from the NRL CHEM2D middle atmosphere model are used to study the hydrogen budget in the equatorial upper stratosphere. Multiyear time series of equatorial upper stratospheric $H_2O + 2*CH_4$ show temporal variations during periods of relative long-term stability in water vapor and methane entering the stratosphere. These variations, which are anticorrelated to CH_4, are quasibiennial and seasonal in nature, and peak near 2 hPa with a magnitude of 3% of the $H_2O + 2*CH_4$ mixing ratio. We find that the ratio of the changes in water vapor to the changes in methane is consistently >2 over the entire equatorial upper stratosphere in HALOE, ACE, and MIPAS data. Ratios of the H_2O to CH_4 changes calculated from the CHEM2D model are similar, but slightly smaller, and the variations in $H_2O + 2*CH_4$ are balanced by nearly equivalent variations in molecular hydrogen. We use this relationship to infer molecular hydrogen mixing ratios from the observations which show that its mixing ratio decreases with altitude above 5 hPa. This net loss in molecular hydrogen drives additional water vapor production so that multiyear average profiles of $H_2O + 2*CH_4$ from HALOE, ACE, and MIPAS show an $\sim$0.4 ppmv increase between 5 hPa and 1.5 hPa, so that total hydrogen is conserved. Collectively, these results illustrate the importance of molecular hydrogen in the equatorial upper stratospheric hydrogen budget.

1.   Introduction

[2]   The hydrogen budget of the stratosphere is dominated by water vapor, methane, and molecular hydrogen so that total long-lived hydrogen, H_y, can be adequately defined as the summation of these three trace gases. Water vapor, methane, and molecular hydrogen enter the stratosphere primarily through the tropical tropopause region, where the seasonal variation in entry water vapor mixing ratios is related to the seasonal variation in tropical tropopause temperatures [*Newell and Gould-Stewart*, 1981; *Mote et al.*, 1996; *Sherwood and Dessler*, 2000; *Holton and Gettelman*, 2001]. Oxidation of methane and molecular hydrogen create a source of water vapor in the upper stratosphere and to a

lesser extent in the lower and middle stratosphere [*Brasseur and Solomon*, 2005]. The net result of these processes is to create a global stratospheric distribution of water vapor with mixing ratios which increase with increasing altitude and latitude [*Remsberg et al.*, 1984; *Harries et al.*, 1996b]. Water vapor affects the stratospheric radiation budget [*Forster and Shine*, 2002], influences the chemical budget of ozone [*Evans et al.*, 1998], and is a tracer of dynamical processes due to its long photochemical lifetime [*Hall and Waugh*, 1997; *Mote et al.*, 1998].

[3]   The chemical process of methane and molecular hydrogen oxidation involves a lengthy series of reactions, but is believed to be reasonably well understood [e.g., *Le Texier et al.*, 1988; *Röckmann et al.*, 2004]. Briefly, methane is oxidized by several chemical reactions to produce water vapor and formaldehyde (CH_2O). CH_2O is then quickly destroyed both by photolysis which yields molecular hydrogen, and by oxidation to produce water vapor. Finally, molecular hydrogen can also be oxidized (in a similar manner as CH_4) into water vapor. The exact amount of water vapor produced by these processes ultimately depends on the difference between the production of molecular hydrogen from CH_2O photolysis and the loss of molecular hydrogen through oxidation and varies somewhat with time of season and location in the stratosphere. If these two effects are balanced, then molecular hydrogen will maintain

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a constant mixing ratio and the quantity $H_2O + 2*CH_4$ will also remain constant. In this case, two molecules of H_2O are produced for each CH_4 molecule lost, and the ratio of the changes of H_2O to CH_4 will also be 2. If, however, the production and loss terms for molecular hydrogen are not balanced, then $H_2O + 2*CH_4$ will vary, and the ratio of H_2O to CH_4 changes will deviate from 2.

[4] Numerous investigations of the stratospheric hydrogen budget using H_2O, CH_4, and H_2 data have taken place shedding detailed information of the relative contributions of the three gases. In particular, several studies of the ratio of the changes of H_2O to CH_4 carried out in the lower and middle stratosphere at various latitudes have shown values near or slightly less than 2 so that molecular hydrogen is in a steady state and $H_2O + 2*CH_4$ is nearly conserved [Dessler et al., 1994; Engel et al., 1996; Abbas et al., 1996; Zöger et al., 1999; Hurst et al., 1999; Nassar et al., 2005]. Studies with data from the Limb Infrared Monitor of the Stratosphere (LIMS) and the Stratospheric and Mesospheric Sounder (SAMS) on Nimbus 7 and from HALOE have revealed significant deviations in the ratio of the changes of H_2O to CH_4 from 2.0 in the equatorial and midlatitude upper stratosphere [Remsberg et al., 1984; Hansen and Robinson, 1989; Remsberg et al., 1996] with values significantly greater than 2. These studies, while motivating further study, were done with limited data or during periods of significant trends in water vapor which might have resulted in an incorrect calculation of the ratio. Modeling results from Le Texier et al. [1988] show that the ratio of the changes of H_2O to CH_4 exceeds 2 in the upper stratosphere when the H_2O source from net H_2 loss is taken into account. Harries et al. [1996a] inferred H_2 in the upper stratosphere and mesosphere from HALOE V19 data based on nonconservation of $H_2O + 2*CH_4$. However, we will show that the Harries study used HALOE H_2O and CH_4 measurements which have biases in the upper stratosphere resulting in an underestimate of H_2 losses in this region. We also note a recent modeling study by Riese et al. [2006] which showed that estimated increases of tropospheric H_2 of $\sim$0.55 ppmv from a possible future hydrogen economy would lead to a $0.3-0.4$ ppmv increase in upper stratospheric H_2O due to increased H_2 oxidation.

[5] This paper uses observational data of water vapor and methane from HALOE on the Upper Atmosphere Research Satellite (UARS) [Russell et al., 1993], ACE on SCISAT-1 [Bernath et al., 2005], and MIPAS on the European Environmental Satellite (Envisat) [Fischer et al., 2008] to study the hydrogen budget in the equatorial upper stratosphere. The data are analyzed over time periods when long-term water vapor changes in the upper stratosphere are small (1996−2007) so that the hydrogen chemistry can be better understood. A large amount of methane oxidation occurs in this region, providing good water vapor to methane fractional response for this study. It is also a region of ascent, and therefore should be only minimally affected by the Lyman-alpha photodissociation of water vapor which occurs in the upper mesosphere, and which could complicate a study of the conservation of $H_y = H_2O + 2*CH_4 + H_2$. While the tropical lower stratosphere retains the signature of seasonal variations in water vapor entering the stratosphere, these variations are small in the upper stratosphere due to mixing of air parcels which occur during transport from the tropical tropopause to the tropical upper stratosphere on time scales of several years. Results from the three instruments highlight the importance of net H_2 loss, in addition to methane oxidation, for the hydrogen budget of the equatorial upper stratosphere.

2. Instruments and Data Products
2.1. HALOE

[6] The HALOE instrument uses solar occultation to measure absorption of solar energy in several broadband and gas filter spectral bands at infrared wavelengths [Russell et al., 1993]. The calculation of the fractional response of solar radiation makes the instrument essentially self-calibrating and results in stable measurements over long periods of time. HALOE measurements are available from October 1991 to November 2005, and the third "public" release data set (version 19) is used for this study.

[7] The H_2O and CH_4 measurements from HALOE have been used extensively in numerous scientific studies related to chemistry, dynamics, and modeling. The H_2O profiles have a vertical resolution of slightly coarser than 2 km. Validation studies by Harries et al. [1996b] confirmed the version 17 H_2O profiles compare favorably with independent measurements and estimated their precision at $\sim$7% and accuracy at $\sim$14% in the upper stratosphere with increasing values toward the top (upper mesosphere) and bottom (near tropopause) of the profiles. The version 17 H_2O errors found from the Harries study are similar to errors for the version 19 data [Kley et al., 2000] and, thus, applicable to this study. The CH_4 measurements have a vertical resolution of $\sim$4.5 km due to the larger retrieval vertical spacing compared to the H_2O retrieval. The version 17 CH_4 measurements were validated by Park et al. [1996] who calculated precision and accuracy values near the stratopause of $\sim$2% and $\sim$6%, respectively. The fractional errors increase slightly both toward the lower stratosphere and middle mesosphere. Version 17 CH_4 errors are also similar to those for the version 19 data (J. M. Russell III, personal communication, 2009).

2.2. ACE-FTS

[8] The ACE-FTS instrument (hereafter referred to simply as ACE) is a high-resolution Fourier Transform Spectrometer which measures atmospheric absorption spectra using solar occultation between 2.2 and 13.3 μm (750–4400 cm^{-1}) [Bernath et al., 2005]. ACE measurements are available from February 2004 to the present, and the version 2.2 data are used for this study.

[9] H_2O data from ACE have been validated by Carleer et al. [2008] by comparisons to H_2O measurements from several spaceborne instruments. The authors concluded that the measurements provided an accurate representation of H_2O to a level better than $5-10\%$ in the stratosphere. The repeatability of the measurement relative to correlative measurements and its high precision ($<$5%) make it very suitable to scientific studies and a good reference measurement. ACE CH_4 data have been validated by De Mazière et al. [2008]. The accuracy of individual CH_4 measurements is within 25% in the middle and higher stratosphere; however this estimate was based primarily on a comparison to HALOE CH_4 which, as will be discussed later, has low

mixing ratios in the tropical upper stratosphere compared to both ACE and Atmospheric Trace Molecule Spectroscopy (ATMOS) data. Comparisons of ACE and MIPAS CH_4 coincident profiles show differences within 10% in the upper stratosphere [*Höpfner et al.*, 2007; *De Mazière et al.*, 2008], suggesting that the 25% accuracy estimate by De Mazière is likely too large. The precision values for ACE H_2O and CH_4 are statistical fitting errors from the least squares based retrieval process [*Boone et al.*, 2005] and have values of 2–3% in the stratosphere. The vertical resolution of H_2O and CH_4 profiles is typically near 4 km.

2.3. MIPAS

[10] The MIPAS instrument is a midinfrared Fourier transform emission spectrometer which measures limb spectra with high spectral resolution over the wavelength range of 4.15 to 14.6 μm. MIPAS measurements have been made from September 2002 to the present, but problems with the interferometer drive unit limited operations during the early 2004 to December 2007 time period [*Fischer et al.*, 2008]. This study uses data produced by a retrieval processor designed at the Institute for Meteorology and Climate Research (IMK) [*von Clarmann et al.*, 2003] and the Instituto de Astrofisica de Andalucia [*Funke et al.*, 2001]. We used data with version numbers V3O_H2O_11 and V3O_H2O_12 for H2O, and V3O_CH4_8 and V3O_CH4_11 for CH4, with the higher version number being used to achieve better data sampling for the last few months of the nineteenth month time series (September 2002 to March 2004) used in the analysis. The differences between these subtypes of V3O retrievals is small (<0.1 ppmv for H_2O and <0.01 ppmv for CH_4), and should have no affect on the results presented here.

[11] IMK/IAA MIPAS H_2O data have been validated versus numerous instruments by *Milz et al.* [2005, 2009], and a comparison to the ACE-FTS instrument is given by *Carleer et al.* [2008]. MIPAS H_2O was found to be ~10% high versus HALOE, while the consistency with ACE-FTS data is on the order of 5% with MIPAS being dryer than ACE-FTS. A northern midlatitudinal error budget analysis by *Milz et al.* [2005] found that the total H_2O random and systematic errors were less than 10% in the stratosphere. Our analysis of the MIPAS H_2O error budget has confirmed that these errors are also valid for tropical data for altitudes above 35 km. CH_4 has been found to be high by 5–10% compared to ACE-FTS in the upper troposphere to middle stratosphere [*Höpfner et al.*, 2007] (also M. Engelhardt et al., Institut fuer Meterologie und Klimaforschung, Universitaet Karlsruhe, unpublished results, 2007). The accuracy of a southern midlatitude CH_4 profile was estimated to range from 10% in the upper troposphere up to ~20% in the upper stratosphere with precision values of ~10% throughout the stratosphere [*Glatthor et al.*, 2005]. Our error analysis has shown that the midlatitude upper stratospheric error values for CH_4 quoted above are very similar to their values at tropical latitudes.

3. Creation of a Uniform Data Set

[12] Comparison of H_2O profiles from HALOE to a variety of coincident H_2O profiles from other instruments [*Harries et al.*, 1996b; *Kley et al.*, 2000; *McHugh et al.*,

2005; *Milz et al.*, 2005; *Lambert et al.*, 2007; *Nedoluha et al.*, 2007] consistently show that HALOE H_2O mixing ratios are biased dry. In the upper stratosphere, the dry bias is a few percent near 5 hPa steadily increasing up to 5–10% near the stratopause. The sense of the altitude-dependent bias is similar between comparisons of HALOE profiles to those from ATMOS, ACE, MIPAS, and AURA-MLS [*Harries et al.*, 1996b; *Kley et al.*, 2000; *McHugh et al.*, 2005; *Milz et al.*, 2005; *Lambert et al.*, 2007; *Nedoluha et al.*, 2007]. A comparison of HALOE CH_4 to ATMOS data [*Park et al.*, 1996] and ACE data [*McHugh et al.*, 2005] shows that the HALOE CH_4 is biased low relative to the other two data sets in the middle and upper stratosphere with the bias increasing with decreasing pressure. As mentioned previously, the ACE H_2O data have a high accuracy (5–10%) in the upper stratosphere [*Carleer et al.*, 2008], while the accuracy of ACE CH_4 is ~10% in the upper stratosphere. Also, comparisons of water vapor between ACE, the Microwave Limb Sounder (MLS) aboard AURA, and the ground-based Water Vapor Millimeter-wave Spectrometer (WVMS) instrument near 20°N show excellent agreement in the absolute values of the water vapor mixing ratio at 50 km [*Nedoluha et al.*, 2009]. Therefore, based on the good absolute accuracy of the ACE measurements along with the similarity of the HALOE H_2O and CH_4 altitude-dependent differences relative to ACE and ATMOS, we have used the ACE data as the standard and have modified the HALOE profiles to remove the relative bias. While we have chosen ACE as the absolute calibration source for CH_4, we do note that comparisons of ACE CH_4 profiles to those from the MIPAS instrument [*Höpfner et al.*, 2007] show a somewhat similar altitude-dependent bias to that of the ACE − HALOE differences in the upper stratosphere, which could suggest that there is some altitude-dependent bias in the ACE data.

[13] The bias correction has been established using equatorial HALOE and ACE data during February and August of 2004 and 2005. Of the four months per year in which both HALOE and ACE made tropical (10°S–10°N) measurements, only February and August yielded an adequate number of profiles (on average, 32 measurements from each instrument per month) for a meaningful comparison. Monthly zonal mean H_2O and CH_4 profiles over 10°S to 10°N were calculated for each of the four months, averaged, and then the average HALOE and ACE profiles were differenced as ACE minus HALOE divided by HALOE. The difference profiles between HALOE and ACE H_2O were then smoothed with an 8 km boxcar average to remove small-scale differences which may be related to differences in vertical resolution. Figure 1 shows the profiles of the 4 month mean HALOE and ACE H_2O and CH_4 data along with the difference profiles. HALOE and ACE CH_4 profiles have less small-scale vertical structure than the H_2O profiles, primarily due to the lower resolution of the CH_4 profiles, hence no smoothing is applied to the CH_4 difference profile. The HALOE and ACE H_2O and CH_4 difference curves based on the equatorial data comparison differ slightly from the results derived from a HALOE correction based on a comparison of HALOE and ACE data at middle and high latitudes from *McHugh et al.* [2005] (not shown), but both reveal altitude-dependent biases which increase (by percentage) with decreasing pressure above ~10 hPa.
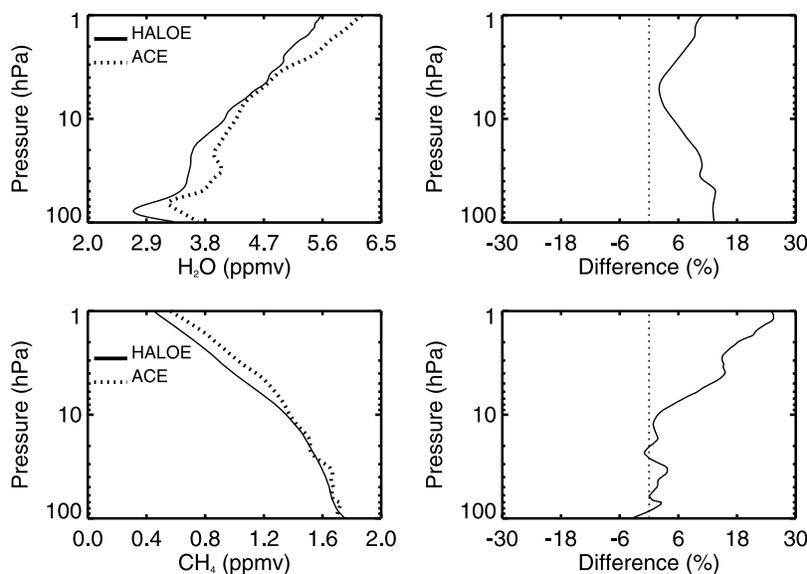
Figure 1. Mean water vapor and methane profiles averaged over February and August of 2004 and 2005 and 10°S–10°N from HALOE and ACE and their percentage differences. (left) Mean profiles (solid line, HALOE; dashed line, ACE), and (right) profiles of their percentage differences where the differences are calculated as (ACE-HALOE)/HALOE. The water vapor differences have been smoothed to account for vertical resolution differences between the two instruments. Unless otherwise indicated, all HALOE data shown and used in this paper are corrected by the fraction shown here.

[14] Comparisons of MIPAS CH_4 data to ACE [*Höpfner et al.*, 2007; Engelhardt et al., unpublished results, 2007] show that the MIPAS data have small positive biases of 5–10% in the lower and middle stratosphere and on the order of 5% in the upper stratosphere. A comparison of MIPAS H_2O to ACE H_2O [*Höpfner et al.*, 2007; *Carleer et al.*, 2008] shows differences of ~5% throughout the stratosphere, with MIPAS generally having lower values relative to ACE. In order to minimize the possible influence of these biases in the current analysis, we have chosen to correct for the biases in the MIPAS H_2O and CH_4 profiles by comparing them directly to the HALOE corrected profiles, which means that the MIPAS corrections are mainly based on ACE. We chose to correct MIPAS to the corrected HALOE (versus MIPAS to ACE) because of insufficient temporal overlap of the MIPAS and ACE data sets. The months in which both HALOE and MIPAS observed the tropics (10°S–10°N) were identified, and monthly mean H_2O and CH_4 mixing ratios corresponding to these months were averaged for each instrument as a function of pressure. The mean H_2O and CH_4 mixing ratios for each instrument were differenced to create H_2O and CH_4 bias curves as was done for the HALOE – ACE comparison (not shown).

[15] The equatorial bias corrections have been used to modify the HALOE and MIPAS H_2O and CH_4 profiles for each data set. All subsequent analyses (unless otherwise indicated) will be performed with the modified HALOE and MIPAS data sets. Figure 2 (top) shows the monthly zonal mean time series of the corrected HALOE, ACE and corrected MIPAS H_2O and two times CH_4 data at 2.2 hPa averaged over 10°S–10°N. Monthly averages are only shown here (and elsewhere) if there are at least 12 individual profiles available. The 2*CH_4 time series show quasi-biennial (QBO) variations which peak near 2.2 hPa in the equatorial upper stratosphere due to the large vertical

gradients in CH_4 [*Cordero et al.*, 1997] and directly relate to the observed QBO variations in H_2O through CH_4 oxidation. An increase in H_2O mixing ratios during the early and middle 1990s is also evident [*Nedoluha et al.*, 2003]. The HALOE and ACE H_2O and CH_4 time series agree well for the overlap time period (2004–2005), though differences of <0.2 ppmv occur. A detailed inspection of individual months over this period shows that when HALOE H_2O is high relative to ACE H_2O, the HALOE CH_4 measurement is low relative to ACE, and vice versa. This anticorrelation of H_2O and CH_4 differences is expected for measurements that are not sampling exactly the same times and locations, and is likely a result of one instrument observing air which has experienced slightly more (or less) methane oxidation. The agreement between HALOE and MIPAS H_2O and CH_4 is generally good, but also shows small differences in H_2O and CH_4 which are anticorrelated in the same sense as seen with the HALOE – ACE comparison. Nevertheless, the good overall agreement in the temporal variations between the three H_2O and CH_4 time series at 2.2 hPa and other pressure levels used in this analysis (1.5, 2.2, 3.2, 4.6, and 6.8 hPa; corresponding approximately to 44.1, 41.2, 38.3, 35.7, and 33.0 km, respectively) provides confidence in the corrections to HALOE and MIPAS.

[16] While the H_2O + 2*CH_4 time series in Figure 2 (bottom) clearly shows smaller variations than either the H_2O or the CH_4 time series, there remain significant variations. Some of the largest variations seem to be primarily quasibiennial in nature and are correlated with the H_2O and CH_4 variations in time with H_2O + 2*CH_4 mixing ratios low when CH_4 is high. The nonconservation of the HALOE upper stratospheric H_2O + 2*CH_4 has also been noted by *Geller et al.* [2002]. Clearly, H_2O + 2*CH_4 is not conserved over this time period in the three data sets,
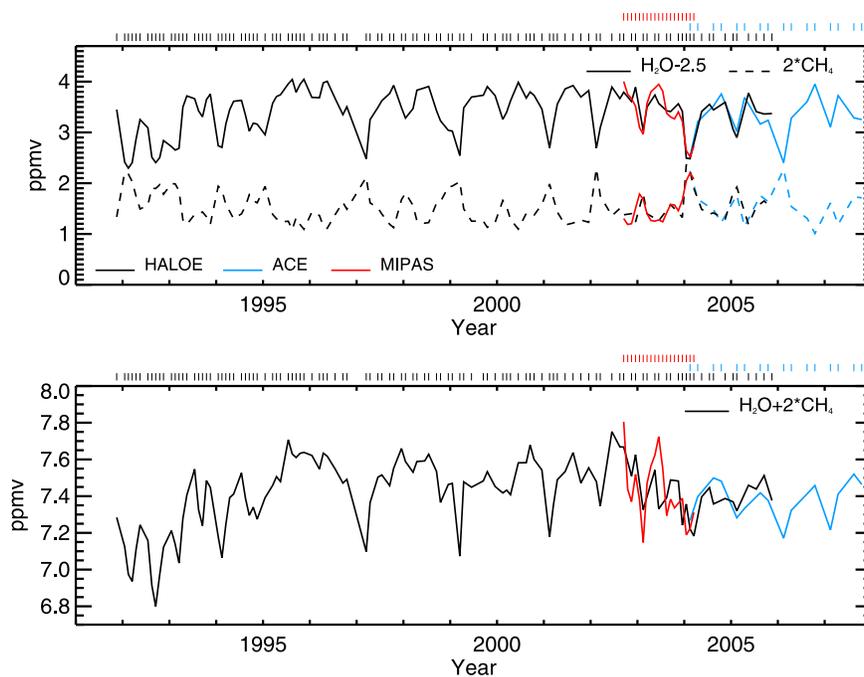
Figure 2. Monthly time series of corrected HALOE (black line), ACE (blue line), and corrected MIPAS (red line) water vapor and (top) two times methane and (bottom) $H_2O + 2*CH_4$ at 2.2 hPa averaged over $10°S - 10°N$. The H_2O time series were shifted to fit the plot. Data markers on the top of each plot show the times of monthly observations (at least 12 profiles required per month) for each instrument (same color connotations).

with the standard deviation of the mean about ±0.2 ppmv, or 3% of the total $H_2O + 2*CH_4$ mixing ratio.

[17] We further illustrate the variations in H_2O, CH_4, and $H_2O + 2*CH_4$ by calculating the amplitudes of the QBO, annual, and semiannual cycles as function of pressure determined by a least squares regression fit to the HALOE data (Figure 3). The regression fit is done with data from 1996 to 2005 over $10°S$ to $10°N$ and included constant, QBO, annual, and semiannual cycle terms. Data from 1991 to 1995 was excluded from the fit to avoid a possible influence from the early 1990s increase in H_2O. The QBO is fit with two empirical orthogonal functions (EOF) which were determined from stratospheric zonal winds above

Singapore and provided by S. Frith (personal communication, 2008).

[18] In the lower and middle stratosphere (below ∼5 hPa), the variations are primarily due to the seasonal cycle of tropical tropopause entry mixing ratios of H_2O which propagate upward in the lower stratosphere. QBO vertical transport anomalies vary the speed at which the seasonal tape recorder signal ascends, and therefore can produce a QBO signal in this region even in the absence of a QBO variation in water vapor entering the stratosphere [*McCormack and Siskind*, 2002]. CH_4 amplitudes are significantly smaller than H_2O amplitudes in the lower stratosphere and thus contribute little to the $H_2O + 2*CH_4$ amplitudes. In the
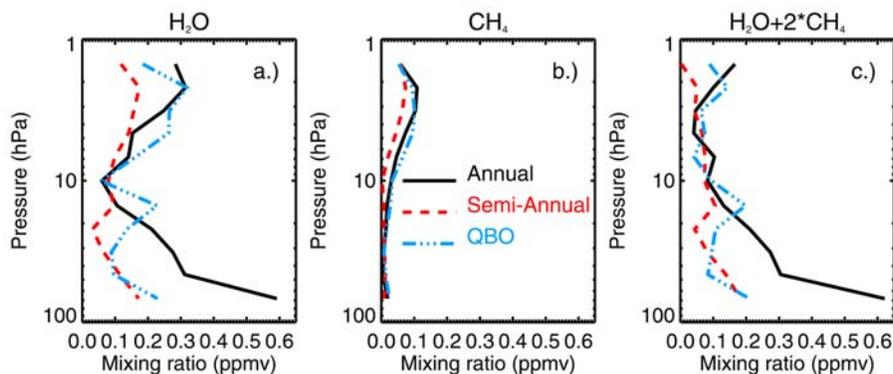

Figure 3. Profiles of annual (solid black line), semiannual (dashed red line), and QBO (dash-dotted blue line) cycle amplitudes from a least squares fit to (a) HALOE H_2O, (b) CH_4, and (c) $H_2O + 2*CH_4$ time series from 1996 to 2005 averaged over $10°S - 10°N$.

Table 1. Single-Level β Values From HALOE Occultation Measurements Over 1996–2005 and 10°S–10°N

Pressure (hPa)	Case a: Reported Errors	Case b: 2*H_2O/ 0.5*CH_4	Case c: 0.5*H_2O/ 2.0*CH_4	Correlation Coefficient
1.5	4.03	2.67	5.91	−0.65
2.2	3.09	2.48	3.72	−0.80
3.2	2.78	2.38	3.08	−0.86
4.6	2.81	2.34	3.03	−0.86

upper stratosphere, however, there are large seasonal cycles in H_2O and CH_4 which are caused by seasonal changes in transport.

[19] The tape recorder signal and all variations related to it decrease with increasing altitude up to ∼10 hPa, but then the variations begin to increase again. Between 1.5 and 10 hPa, the variations in H_2O are anticorrelated with variations in CH_4, since parcels which have experienced more CH_4 oxidation will necessarily have more H_2O. Given complete CH_4 oxidation, one might therefore expect that the variation in H_2O + 2*CH_4 would continue to decrease with increasing altitude in the upper stratosphere. However, as is shown in Figure 3c, this is not the case.

4. Correlation Analysis

[20] We examine the H_2O/CH_4 relationship by studying the correlation of H_2O to CH_4. We then define the negative of the slope of the changes of H_2O to the changes of CH_4 as β [Le Texier et al., 1988],

$$\Delta[H_2O] = -\beta * \Delta[CH_4]. \qquad (1)$$

We calculate β using regression fits both for H_2O versus CH_4 changes at one pressure level (single-level β) and for H_2O versus CH_4 changes over a range of pressures (multilevel β). The single-level β values are particularly sensitive to assumptions about measurement precision, while the multilevel β values are most sensitive to level-dependent systematic errors in the measurements. Unless chemistry changes quickly with altitude, the methods should give similar results.

[21] For calculations of β on one pressure surface, measurements of a sufficient time period are necessary so that the CH_4 changes are large enough relative to the measurement precision error in order to calculate a linear least squares fit line to the H_2O/CH_4 relationship that is not simply dependent on the errors in CH_4. Since the transport time scales that cause the largest variations in CH_4 are related to seasonal and QBO variations, at least 1–2 years of data is suitable, though shorter time periods are possible if the measurement precision error is small compared to the size of the CH_4 variations. This time requirement is not necessary for multilevel β calculations since large CH_4 changes occur over range of pressures. It is also important that the β calculation take place over a time period when the H_2O/CH_4 relationship is not greatly affected by nonconservative processes to either H_2O or CH_4, for example a long-term trend in stratospheric entry mixing ratios of H_2O or CH_4 that propagates to the upper stratosphere. There was no clear trend in H_2O and CH_4 in the upper stratosphere between

1996 and 2002 [Nedoluha et al., 2003]. During 2001, an influx of very dry air was observed in the equatorial lower stratosphere [Randel et al., 2004]; however, the change in water vapor in the upper stratosphere (at most a few tenths of a ppmv) appears to be much smaller than the early 1990s increase of nearly 1 ppmv. We therefore included upper stratospheric HALOE data from 1996 to 2005 in the β analysis. Additionally, we separately analyze the time period 2004–2005 for a direct comparison to the ACE data.

4.1. Single-Level Correlation Analysis

[22] For the regression at one pressure level, we calculate the mean H_2O and CH_4 mixing ratios for all measurements with observation latitudes between 10°S and 10°N and over 1996 to 2005. A least squares regression to determine a best straight-line fit to the H_2O to CH_4 changes is performed using the "fitexy.pro" routine in the Interactive Data Language (IDL) [Press et al., 1992], and the negative of the slope of the best fit line is taken as the β value (equation (1)). The fit is sensitive to the random uncertainties in both the H_2O and CH_4 measurements which for H_2O profiles are taken from Harries et al. [1996b] and for CH_4 profiles from Park et al. [1996]. Given that random uncertainties are inherently difficult to quantify, we calculate β for three different estimates of random error, one for the reported uncertainties (case a), one with the CH_4 uncertainties halved and the H_2O uncertainties doubled (subsequently referred to as a 4:1 H_2O/CH_4 random error ratio) (case b), and one with the H_2O uncertainties halved and the CH_4 uncertainties doubled (a 1:4 H_2O/CH_4 random error ratio) (case c). We note that β calculations done by doubling both the H_2O and CH_4 random errors (or for other cases where the H_2O/CH_4 error ratio reduces to 1:1) would yield the same β value as for the 1:1 H_2O/CH_4 error ratio case.

[23] Values of β were calculated on four pressure surfaces between 1.5 and 4.6 hPa, and for the three cases of error ratios discussed above. These pressure levels were chosen to sample the region of the tropical upper stratosphere where the H_2O + 2*CH_4 variations increase with decreasing pressure above 5 hPa (Figure 3c). For pressures greater than ∼5 hPa, the variations in methane oxidation (and, hence, CH_4 mixing ratios) are small and there may remain some small seasonal variations in H_2O mixing ratios which originate at the tropical tropopause, hence calculations of β are difficult to interpret. β calculations are also not possible above 1.5 hPa because most of the CH_4 rich air from the tropical lower stratosphere has oxidized by the time it reaches the stratopause. The results of the β calculations are summarized in Table 1. The correlation coefficients of the H_2O to CH_4 changes for each pressure are also shown in Table 1 and in the remaining tables in this article.

[24] In Figure 4a, we show an example of the regression plot for calculating β values at 1.5 and 2.2 hPa. The data points corresponding to individual occultation measurements at the 1.5 hPa pressure level are shown in blue, while the points at 2.2 hPa are shown in red. The linear least squares regression fit lines shown here (same color connotations) are calculated by assuming half the CH_4 random error and twice the H_2O random error at this level. The actual error values used for the regressions were 1.3% for CH_4 and 15.7% for H_2O at 1.5 hPa and 1.4% for CH_4 and 15.3% for H_2O at 2.2 hPa. The β value was 2.67 ± 0.02 at
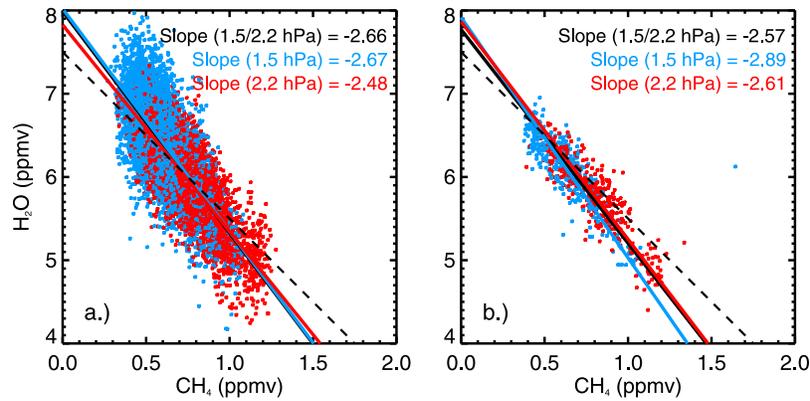
Figure 4. Water vapor versus methane at (a) 1.5 and 2.2 hPa measured by HALOE from 1996 to 2005 and (b) 1.5 and 2.2 hPa measured by ACE from 2004 to 2007. The data points and linear least squares fit line to the data are shown in blue for 1.5 hPa and in red for 2.2 hPa. The linear least squares fit line through the cumulative distribution of points at 1.5 and 2.2 hPa is shown in black. All data shown are for the latitude range of $10°S-10°N$. The slopes of the linear least squares fit lines are shown in the top right-hand corner of each plot. The dashed lines have slopes of -2.0.

1.5 hPa and 2.48 ± 0.01 at 2.2 hPa, where the uncertainty in β is due to the linear fitting error. Given the large number of points, the fitting error represents an insignificant component in the total uncertainty in β. For comparison to the linear least squares fit lines, a dashed line with a slope of -2.0 representing the conservation of $H_2O + 2*CH_4$ and assumed steady state H_2 mixing ratio is also shown in Figure 4a.

[25] If the rate of H_2 production via CH_4 oxidation is balanced by the rate of H_2 oxidation to H_2O, then two molecules of H_2O will be produced for each CH_4 molecule lost. In terms of a β value, β would then be equal to exactly two. From the HALOE analysis, the β values are all greater than 2.0 (taking into account the small fitting error) for all pressure levels and H_2O/CH_4 random error ratio cases, implying that more than two molecules of H_2O are produced for each CH_4 molecule lost. Since the only other reservoir of hydrogen is H_2, this suggests that there is a net loss of H_2 in the equatorial upper stratosphere which, in addition of CH_4 oxidation, drives the production of H_2O. It is also noted that an altitude dependence is suggested in the HALOE β values, with higher values at smaller pressures. This altitude dependence may reflect variations in the balance between H_2 production and loss as a function of altitude.

[26] The single-level β values from Table 1 show large variability for the three different random error ratio cases. These β values are calculated from individual occultation measurements of H_2O which are often noisy in the upper stratosphere. The calculation of β from noisy data will result in a large variation in values, depending on the random error estimate. We therefore also calculate β from month-to-month changes in H_2O and CH_4 instead of from the occultation measurements for the three random error cases described above (Table 2). This averaging will have the effect of removing most of the random variability in the data while still retaining the month-to-month changes. We use the same random errors in H_2O and CH_4 as for the occultation data analysis but now reduce them by the square root of the average number of HALOE profiles per month. The β values show much smaller variations for the three

H_2O/CH_4 random error ratio cases which results from an averaging of the noisy individual measurements. We note that the linear fitting errors using monthly means are similar to those found using the occultation data ($0.01-0.02$ at 1.5 hPa). This analysis emphasizes the potential effect of measurement noise on determining the slope from a linear least squares fit line. Also, for a given H_2O/CH_4 random error ratio, the calculated β value should be nearly identical using either individual measurements or for data averaged over time (e.g., monthly). A comparison of the β values calculated from the occultation data (Table 1) and the monthly data (Table 2) shows that the best agreement is achieved by assuming half the CH_4 random error and twice the H_2O random error (case b). These results suggest that the ratio of H_2O to CH_4 random errors may be larger than have been previously reported [*Harries et al.*, 1996b; *Park et al.*, 1996].

[27] Correlation plots of ACE H_2O and CH_4 are made in a similar manner to the HALOE analysis except the data period is from 2004 to 2007. Due to the inclination of the ACE orbit, the data sampling in the tropics is sparser than that of HALOE. Figure 4b shows the correlations of the ACE H_2O and CH_4 at 1.5 and 2.2 hPa where a H_2O/CH_4 random error ratio of 1:1 has been used for the regression fits. The calculated β was 2.89 ± 0.03 at 1.5 hPa and 2.61 ± 0.10 at 2.2 hPa, statistically greater than 2.0 and persistent for the later time period compared with the HALOE analysis.

[28] The β values were calculated at the pressure levels from 1 to 4.6 hPa (Table 3). We only show results where the

Table 2. Single-Level β Values From HALOE Monthly Mean Measurements Over 1996–2005 and $10°S-10°N$

Pressure (hPa)	Case a: Reported Errors	Case b: $2*H_2O/$ $0.5*CH_4$	Case c: $0.5*H_2O/$ $2.0*CH_4$	Correlation Coefficient
1.5	2.87	2.74	3.11	−0.93
2.2	2.62	2.53	2.73	−0.96
3.2	2.44	2.37	2.50	−0.97
4.6	2.57	2.33	2.70	−0.92

Table 3. Single-Level β Values From ACE Occultation Measurements Over 2004–2007 and 10°S–10°N

Pressure (hPa)	Case a: Reported Errors	Case b: 2*H_2O/ 0.5*CH_4	Case c: 0.5*H_2O/ 2.0*CH_4	Correlation Coefficient
1.0	3.54	2.75	3.68	−0.81
1.5	2.89	2.50	2.99	−0.89
2.2	2.61	2.23	2.75	−0.88
3.2	2.30	2.03	2.48	−0.89
4.6	2.54	2.03	2.92	−0.81

absolute value of the correlation coefficient is at least 0.65 in this study. The β values are all statistically greater than 2.0 for all pressure levels except for the 4:1 H_2O/CH_4 random error ratio case at 4.6 hPa and also show an altitude dependence in the same sense as observed by HALOE. β values were also calculated for the overlapping time period of HALOE and ACE observations of 2004–2005. Good agreement between the HALOE and ACE β values were found for 1.5–4.6 hPa.

[29] The MIPAS H_2O and CH_4 measurements were analyzed to calculate β values for pressures between 1 and 4.6 hPa. Monthly mean residuals for H_2O and CH_4 were calculated for the 19 months of observations available between September 2002 and March 2004. For the linear fit calculation, the random uncertainty for H_2O and CH_4 is determined by taking the root-sum-square of the individual random error sources for the H_2O and CH_4 measurements, which include detector noise, uncertainties of parameters in the retrieval calculation, and line-of-sight pointing errors. Since random errors are not currently available for every measurement, an individual profile of random error sources was used in this analysis. The relative random errors between the various error sources for this one profile should be representative of tropical conditions. The calculated β values for each pressure level are shown in Table 4. Reasonable agreement between the MIPAS β values and those from HALOE and ACE is apparent; however, the monotonic altitude dependence observed in the HALOE and ACE β is not seen in the MIPAS values. This discrepancy could be related to the short time period used for the MIPAS analysis. The actual random errors for the 1:1 H_2O/CH_4 random error ratio case were 7–10% for CH_4 and 5–10% for H_2O for the range of pressures in Table 4, which were reduced by the square root of the average number of MIPAS profiles per month for the regression calculations. The regression fitting errors ranged from 0.01 to 0.07 for the five pressures and three random error ratio cases.

[30] Having calculated a range of β values, we now address mechanisms which may affect β in the tropical upper stratosphere.

4.1.1. Propagation of Lower/Middle Stratospheric H_2O and CH_4 Variations

[31] As air from the tropical tropopause propagates upward, we would expect the tape recorder signal to decrease with increasing altitude, and indeed the H_2O variations observed in the HALOE data generally decrease from 68 to 10 hPa, and the H_2O + 2*CH_4 variations decrease from 68 to 5 hPa (see Figure 3). But from 5 hPa to 1 hPa, where variations in CH_4 begin to become significant relative to those in H_2O, variations in H_2O and in H_2O + 2*CH_4 generally increase. Under some circumstances, an increase

in temporal variation in H_2O + 2*CH_4 with increasing altitude does occur in the lower stratosphere, such as the increasing QBO variations which *McCormack and Siskind* [2002] attribute to the interaction of QBO-induced circulation anomalies with the seasonal variations in H_2O mixing ratios. However, while some of the variations in H_2O + 2*CH_4 in the upper stratosphere are certainly driven by the variations in entry level H_2O, we argue that they would likely be small in the tropical upper stratosphere due to the diminished amplitude of the tape recorder signal at 10 hPa compared to at 68 hPa (see Figure 3a).

[32] It is not possible remove the H_2O tape recorder signal from the total H_2O variations in the upper stratosphere due to a blending of the tape recorder with H_2O variations related to seasonal and QBO fluctuations in transport; however, we can estimate an upper limit to the magnitude of the H_2O tape recorder on β in the upper stratosphere by taking the annual amplitude of H_2O + 2*CH_4 at 10 hPa and then using this value at pressures above 10 hPa. The H_2O + 2*CH_4 signal is used instead of H_2O to estimate the H_2O tape recorder because a small portion of the annual cycle in H_2O at 10 hPa is from an annual transport cycle, which is canceled out in H_2O + 2*CH_4. This estimate will be an upper limit because the tape recorder signal should continue to decay above 10 hPa. If we take the tape recorder amplitude at 10 hPa of ±0.08 ppmv (Figure 3c) and subtract it from the H_2O mixing ratio at 1.5, 2.2, 3.2, and 4.6 hPa, we can estimate the maximum effect the tape recorder will have on the H_2O/CH_4 relationship. The H_2O/CH_4 regression was carried out the same as before, but the H_2O mixing ratios were altered by the magnitude of the annual cycle corresponding to the time of the year of the measurement. Since the phase of the annual cycle is also not known, regressions were calculated for a range of phases. The calculated β value remained above 2.0 for all regressions. For example, β at 3.2 hPa ranged from 2.51 to 2.24, and β at other pressures had similar variations as a function of the phase of the annual cycle. Therefore, we conclude that tape recorder effects cannot fully account for the observed variations in H_2O + 2*CH_4 in the equatorial upper stratosphere, although it is possible that they could slightly modify β as a function of season.

4.1.2. Systematic Data Uncertainties

[33] Systematic fractional biases in either H_2O or CH_4 can change the quantity H_2O + 2*CH_4 and its variations. Although we have attempted to adjust the HALOE H_2O and CH_4 to account for low mixing ratios relative to ACE and other data sets, we cannot be certain of the absolute accuracy of the ACE data and, thus, must consider that

Table 4. Single-Level β Values From MIPAS Monthly Mean Measurements Over September 2002 to March 2004 and 10°S–10°N

Pressure (hPa)	Case a: Reported Errors	Case b: 2*H_2O/ 0.5*CH_4	Case c: 0.5*H_2O/ 2.0*CH_4	Correlation Coefficient
1.0	3.16	2.61	3.29	−0.86
1.5	2.59	2.26	2.69	−0.92
2.2	3.27	3.06	3.29	−0.96
3.2	2.67	2.46	2.71	−0.94
4.6	3.16	2.79	3.23	−0.84

Table 5. Multilevel β Values From HALOE Over 1996–2005, ACE Over 2004–2007, and MIPAS Over September 2002 to March 2004 Between 10°S and 10°N[a]

Pressure Range (hPa)	HALOE	ACE	MIPAS
1.5–4.6	2.65 (−0.93)	2.48 (−0.95)	2.77 (−0.98)
1.5–2.2	2.66 (−0.77)	2.57 (−0.88)	2.85 (−0.95)
2.2–3.2	2.48 (−0.87)	2.64 (−0.91)	2.77 (−0.96)
3.2–4.6	2.38 (−0.90)	2.32 (−0.89)	2.83 (−0.95)

[a]Correlation coefficients shown in parentheses.

H_2O and CH_4 might still have systematic fractional uncertainties which could result in changes to the variations in $H_2O + 2*CH_4$. In order to reduce the variations of $H_2O + 2*CH_4$, we can infer from Figure 2 that CH_4 would need to be increased, H_2O decreased, or some combination of these two.

[34] The β values of 2.0 could be obtained at 2.2, 3.2, and 4.6 hPa by either reducing H_2O by 20%, increasing CH_4 by 25%, or a combination of the two (e.g., −10% for H_2O, +12.5% for CH_4). The intermediate case with ∼10% systematic error for each gas is comparable in value to the total reported systematic data uncertainties [*Harries et al.*, 1996b; *Park et al.*, 1996] hence, given that we have increased the HALOE H_2O mixing ratios by ∼5% to bring them closer to the ACE and ATMOS values, this is certainly not an implausible explanation for the $H_2O + 2*CH_4$ variations when we consider the HALOE data only. However, given the preponderance of quantitative evidence suggesting that the HALOE water vapor measurements are biased slightly low (see section 3), it seems unlikely that they are actually too high. It is also noted that similar arguments can be made regarding the effect of potential systematic biases on β values from the ACE and MIPAS data.

4.1.3. Vertical Resolution Differences

[35] Vertical resolution differences between HALOE H_2O and CH_4 are another factor that could affect $H_2O + 2*CH_4$. The vertical resolution of the HALOE H_2O measurements is slightly over 2.0 km while the CH_4 measurements have a 4.5 km resolution. In practice, these measurements should have the same vertical resolution if they are combined into the quantity $H_2O + 2*CH_4$. We note that this issue does not affect MIPAS and ACE since these H_2O and CH_4 profiles have the similar vertical resolutions.

[36] We have estimated this effect by smoothing the H_2O profiles to 4.5 km to match the CH_4 vertical resolution. This smoothing is achieved by convolving a 4 km wide Gaussian function with the H_2O profiles resulting in a net vertical resolution of ∼4.5 km. Then, regression analyses were carried out on the individual H_2O and CH_4 measurements to calculate β values. The β values were reduced from 2.67 to 2.42 at 1.5 hPa and from 2.48 to 2.31 at 2.2 hPa, for example, but remained significantly above 2.0 throughout the upper stratosphere.

4.2. Multilevel Correlation Analysis

[37] We now consider the calculation of β using multiple pressure levels (multilevel β values). Combining different pressure levels has the advantage of better covering the H_2O and CH_4 variations, which will make the β calculation less dependent on estimated random errors. However, calculating a β by combining data from different pressure levels does

make the calculation sensitive to any pressure-dependent systematic error in the measurements. In the absence of measurement error, and provided the true β is similar between levels, the two methods should give very similar results. For a larger separation of the pressure surfaces, the H_2O and CH_4 changes represent the average changes over several pressure surfaces due to various transport processes of possibly varying type and magnitude, and the calculated β will have an intermediate value between the single-level β values bounding the pressure range.

[38] In Table 5 we show β values calculated between several pressure surfaces for HALOE, ACE, and MIPAS data. For the multilevel analysis, only the data at the two pressure levels which define the pressure range are used; data for intermediate pressure levels are not included in the regression. Figure 4a shows the distribution of HALOE H_2O and CH_4 used to calculate β between 1.5 and 2.2 hPa using a 4:1 H_2O/CH_4 random error ratio. The linear least squares fit line to the cumulative distribution of data points at 1.5 and 2.2 hPa is shown by the solid black line. The calculated β of 2.66 between 1.5 and 2.2 hPa falls in between the single-level β values calculated using a 4:1 H_2O/CH_4 random error ratio at 1.5 and 2.2 hPa, thus this choice of random errors and bias correction to the HALOE data is self-consistent. Figure 4b shows the distribution of ACE H_2O and CH_4 used to calculate β between 1.5 and 2.2 hPa using a 1:1 H_2O/CH_4 random error ratio. This random error ratio is used because it leads to the best agreement between the ACE single and multilevel β values between 1.5 and 4.6 hPa. A 4:1 H_2O/CH_4 random error ratio was used for the MIPAS β value calculations. The ACE and MIPAS results are similar to those from HALOE. This similarity is partially imposed because we have bias-corrected the HALOE and MIPAS profiles to match the ACE data. The consistency between the multilevel and single-level calculations is, however, not imposed, hence the general agreement between these values and those of the single-level calculations is encouraging. All the results show β values above 2.0.

[39] In Figure 5 we illustrate the importance of bias correcting the HALOE data to ACE. The linear least squares fit lines shown here are calculated by assuming half the CH_4 random error and twice the H_2O random error at each level. Figure 5a shows the distribution of HALOE H_2O versus CH_4 data at 1.5 and 4.6 hPa for uncorrected (i.e., version 19) data. The calculated β values are 3.02 and 2.63 at 1.5 and 4.6 hPa, clearly larger than the value of 2.10 for the multilevel case of 1.5 to 4.6 hPa. It is also noted that single-level β values for intermediate pressures between 1.5 and 4.6 hPa also have values exceeding 2.0. Figure 5b shows a similar plot but for HALOE data which have been bias corrected to ACE as described in section 3. Here, as expected, the multilevel β over the pressure range has an intermediate value between the two single-level β values. The similarity of the single and multilevel β values suggests that bias correcting the HALOE data to ACE has produced a more geophysically consistent data set.

5. CHEM2D Modeling

[40] Output from the Naval Research Laboratory (NRL) zonally averaged CHEM2D model has been used to inves-
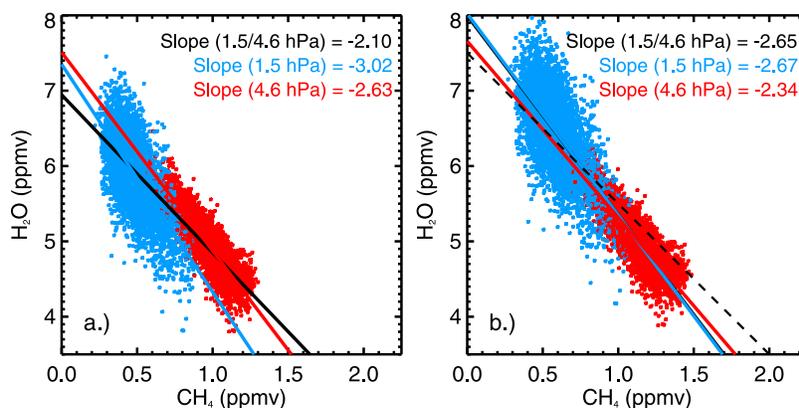
Figure 5. Water vapor versus methane at 1.5 and 4.6 hPa measured by HALOE from 1996 to 2005 using (a) version 19 data and (b) data bias corrected to ACE. The data points and linear least squares fit line to the data are shown in blue for 1.5 hPa and in red for 4.6 hPa. The linear least squares fit line through the cumulative distribution of points at 1.5 and 4.6 hPa is shown in black. All data shown are for the latitude range of 10°S–10°N. The slopes of the linear least squares fit lines are shown in the top right-hand corner of each plot. The dashed line has a slope of −2.0.

tigate the hydrogen chemistry of the upper stratosphere. CHEM2D is a global middle atmosphere model extending from the surface to ∼120 km altitude with interactive radiative, photochemical and dynamical schemes. The version of CHEM2D used in the present study has 88 vertical levels with a vertical grid spacing of 1.5 km [*McCormack et al.*, 2007]. CHEM2D has been shown to successfully simulate the general distribution and variability of tracers such as H_2O, CH_4, and N_2O [*Summers et al.*, 1997; *McCormack and Siskind*, 2002]. Here we analyze monthly zonal mean H_2O, CH_4 and H_2 fields from a 30 year CHEM2D simulation in which the entry value of H_2O mixing ratio at the tropical tropopause (17 km) varies sinusoidally with an amplitude of 1.5 ppmv about a mean value of 3.5 ppmv. No trends or other interannual variations in H_2O entering the middle atmosphere from the tropical troposphere are present. Model CH_4 mixing ratios are held fixed at 1.75 ppmv in the troposphere throughout the simulation. The model includes an interactive parameterization of the QBO in equatorial stratospheric winds. The QBO modulates the strength of the modeled tropical up-welling in the lower stratosphere and produces a small QBO in model H_2O and CH_4 [*McCormack and Siskind*, 2002].

[41] Figure 6 shows H_2O, CH_4, $H_2O + 2*CH_4$, H_2, and $H_2O + 2*CH_4 + H_2$ at a pressure of 1.4 hPa for years 20–25 of the simulation averaged over 10°S to 10°N. While the variability in H_2O and CH_4 is somewhat different than that seen in the HALOE data, the CHEM2D model shows that $H_2O + 2*CH_4$ has time variations which are anticorrelated with the CH_4 variations in the same sense as the observations. As expected, the $H_2O + 2*CH_4$ variations are also anticorrelated with variations in H_2, such that $H_2O + 2*CH_4 + H_2$ is nearly constant in time. The remaining fluctuations in $H_2O + 2*CH_4 + H_2$ are due to seasonal variations in the H_2O tape recorder signal; therefore, we have used this time series to estimate the tape recorder signal by calculating the residuals from the mean $H_2O + 2*CH_4 + H_2$ mixing ratio. This tape recorder estimate is subtracted from the H_2O time series at each pressure, and

regression fits are made to the H_2O versus CH_4 changes. The calculated single-level β values based on the H_2O and CH_4 variations at 1.2, 1.4, 2.1, 3.0, and 4.4 hPa for years 20–25 are 2.42, 2.38, 2.29, 2.20, and 2.11, respectively. The calculated multilevel β value between 1.2 and 4.4 hPa is 2.27, or roughly an average of the single-level β values over this pressure range. These values are all greater than 2, but they are somewhat smaller than the values determined from observations. We would expect that the β values are a function of both circulation and chemistry, hence even if the model chemistry is correct, it is possible that the disagreement in the model and observed β values may be attributed to differences between the CHEM2D circulation and the actual circulation. The single-level β values also show a clear altitude dependence after the effects of the H_2O tape recorder were removed in a similar sense to behavior of the HALOE and ACE β values. A greater proportion of H_2 loss versus production is likely responsible for most of the altitude dependence though some may also be due other transport processes not properly simulated in the model.
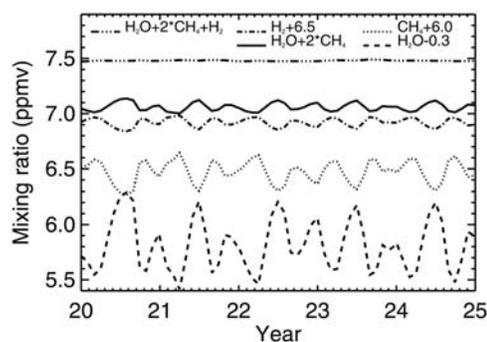

Figure 6. Time series of water vapor, methane, molecular hydrogen, $H_2O + 2*CH_4$, and $H_2O + 2*CH_4 + H_2$ at 1.4 hPa averaged over 10°S–10°N from CHEM2D. The time series shown is for years 20–25 of a 30 year simulation. Note that some of the time series have been shifted to fit the plot.
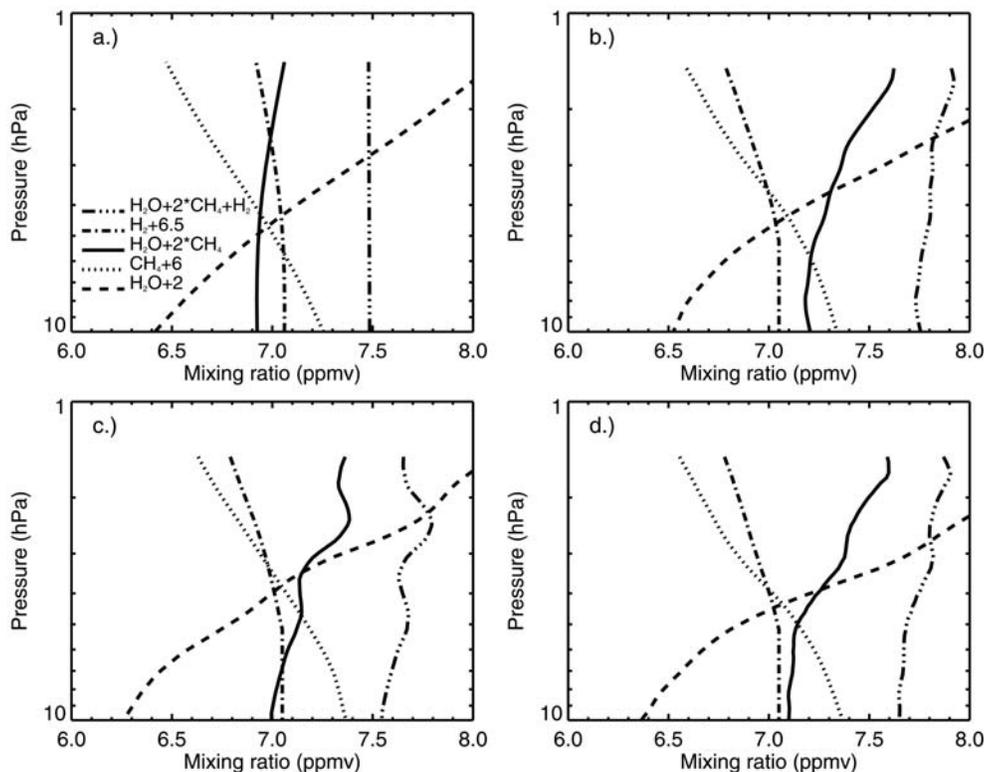
Figure 7. Mean profiles of water vapor, methane, molecular hydrogen, $H_2O + 2*CH_4$, and $H_2O + 2*CH_4 + H_2$ from (a) CHEM2D averaged over years $20-25$ of a 30 year simulation, (b) HALOE averaged over $1996-2005$, (c) ACE averaged over $2004-2007$, and (d) MIPAS averaged over October 2002 to September 2003. All profiles were averaged over $10°S-10°N$, and the water vapor, methane, and molecular hydrogen profiles were shifted to fit the plots. The line description for each profile is shown in Figure 7a. We note that CHEM2D simulates each component of $H_2O + 2*CH_4 + H_2$ explicitly, while H_2 is inferred from the observations using equation (3).

[42] Mean profiles of the relevant hydrogen parameters from CHEM2D averaged over years $20-25$ and $10°S$ to $10°N$ are shown in Figure 7a. Similarly calculated profiles from the HALOE, ACE, and MIPAS observations shown in Figures 7b–7d will be discussed later. As expected from the CHEM2D single-level β values >2, a slight positive vertical gradient is observed in $H_2O + 2*CH_4$ above ~5 hPa. The increase in model $H_2O + 2*CH_4$ of about 0.15 ppmv between the 5 and 1.5 hPa levels is balanced by a comparable decrease in H_2, suggesting that at least 0.15 ppmv more H_2 is lost through oxidation than produced from CH_2O photolysis in the equatorial upper stratosphere.

6. Measurement Time Series and Vertical Profiles

[43] The above results highlight the nonconservation of $H_2O + 2*CH_4$ in the equatorial upper stratosphere which results from H_2 not being in steady state. As expected, model results from CHEM2D show $H_2O + 2*CH_4$ variations which are balanced primarily by H_2 variations, so that total hydrogen, H_y, is conserved by adding H_2 to $H_2O + 2*CH_4$,

$$H_y = H_2O + 2*CH_4 + H_2. \qquad (2)$$

Variations in total hydrogen can then be calculated as a function of pressure and time from the observational data by relating the H_2 term in equation (2) with the variations in $H_2O + 2*CH_4$. We believe that this is a valid approach in light of the CHEM2D results and having ruled out other potential sources of the $H_2O + 2*CH_4$ variations. If the H_2 term is expanded into a mean and residual term and equation (1) is substituted in (2), then H_y at pressure level p_i can be expressed solely in terms of H_2O, CH_4, and the β values (along with an assumed constant H_2 mixing ratio of 0.55 ppmv at 5 hPa (level 1 in (3)),

$$H_y(p_i, t) = H_2O(p_i, t) + 2*CH_4(p_i, t) + \langle H_2(7\ hPa) \rangle$$
$$+ \sum_{i=i,j} \{[0.5*(\beta(p_i) + \beta(p_{i-1})) - 2]*[\langle CH_4(p_i) \rangle$$
$$- \langle CH_4(p_{i-1}) \rangle]\} + (\beta(p_i) - 2)*dCH_4(p_i, t). \qquad (3)$$

The third term of equation (3) is the long-term average H_2 mixing ratio at 5 hPa (taken from in situ measurements showing average H_2 mixing ratios of 0.55 ppmv in the $8-10$ hPa range [*Zöger et al.*, 1999; *Rohs et al.*, 2006]), while the fourth term is the summation of the changes in the long-term average CH_4 mixing ratio between 5 hPa and the
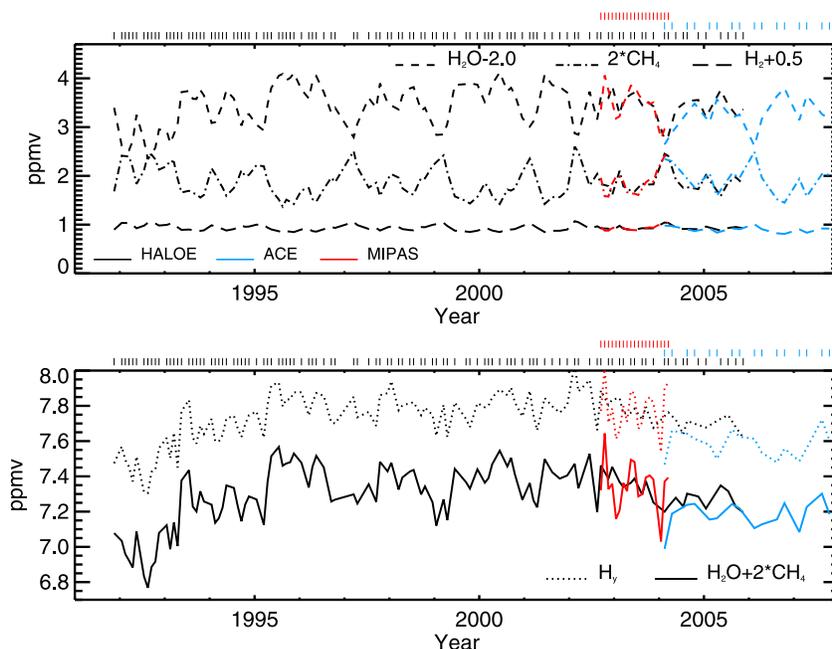
Figure 8. Time series of corrected HALOE (black line), ACE (blue line), and corrected MIPAS (red line) (top) water vapor, two times methane, and inferred molecular hydrogen and (bottom) $H_2O + 2*CH_4$ and H_y at 3.2 hPa averaged over $10°S - 10°N$. The H_2O and H_2 time series were shifted to fit the plot. Data markers on the top of each plot show the times of monthly observations (at least 12 profiles required per month) for each instrument (same color connotations).

pressure of interest multiplied times ($\beta - 2$) where β is an average of the value at the chosen pressure and one level below. We choose 5 hPa as the "reference" pressure in the calculation since $H_2O + 2*CH_4$ has minimal variations near this pressure and because this was the highest pressure at which β calculations were possible. For the fifth term, we have calculated CH_4 monthly residuals from the overall time mean for a particular instrument. Finally, the β values in the fourth term are pressure dependent between 5 hPa and the chosen pressure, while the β value in the fifth corresponds to the pressure at which H_y is calculated.

[44] Although time series of H_y can be calculated using the β values calculated from the correlation analysis, in this calculation, we search for a value of β such that H_y at each level is conserved. The HALOE data were used to calculate the β value that minimizes the variations in H_y (hereafter termed the "residual" β value) since these data have the longest record of simultaneous H_2O and CH_4 observations in this region of the tropical upper stratosphere and, thus, should provide the best long-term average β value. The time series were again restricted to 1996–2005 in order to avoid a possible influence of the early 1990s increase in upper stratospheric H_2O on the residual β value calculations. Multiple time series of H_y were calculated at each pressure level (1.5, 2.2, 3.2, and 4.6 hPa) using equation (3) where the β value was varied from 2.0 to 4.0 in increments of 0.02. Then, standard deviations of the H_y time series at each pressure level were calculated in order to find the β (at each pressure) that gave the smallest standard deviation. The calculated residual β values were 2.66, 2.56, 2.38, and 2.30 for 1.5, 2.2, 3.2, and 4.6 hPa, respectively. These β values result in a reduction of the standard deviation in H_y of 4% at 4.6 hPa up to a maximum of 19% at 2.2 hPa compared to

time series of H_y computed with a β value of 2. Time series of H_y for the HALOE, ACE, and MIPAS data are then calculated at the four pressure levels using the HALOE derived residual β values.

[45] Figures 8 shows time series of H_y at 3.2 hPa averaged over $10°S$ to $10°N$ along with time series of H_2O, $2*CH_4$, inferred H_2, and $H_2O + 2*CH_4$ where the H_2 mixing ratios are calculated from the last three terms of equation (3). The H_y and $H_2O + 2*CH_4$ time series are presented with a smaller vertical scale in order to better show the small variations. Figure 8 shows that the variations seen in H_y are noticeably reduced compared with those in the $H_2O + 2*CH_4$ time series. The ACE and MIPAS H_y time series also show an overall reduction in total variability when the residual β values HALOE are used and overlap with the HALOE H_y time series. The overall agreement in H_y between the three instruments is very encouraging and provides confidence in the mixing ratio of total hydrogen and, as shown later, stratospheric entry level H_2O. These results highlight the importance of understanding variations in H_2 as well as those of H_2O and CH_4 in this region of the atmosphere.

[46] Least squares regression fits were done to the HALOE H_y time series over 1996–2005 averaged over $10°S$ to $10°N$ as was done in Figure 3 for H_2O, CH_4, and $H_2O + 2*CH_4$. Figure 9 shows the amplitudes of the QBO, annual, and semiannual cycles as a function of pressure calculated from the fit. Since H_y is only calculated for pressures less than 5 hPa, the amplitudes for $H_2O + 2*CH_4$ are shown below this pressure level. A comparison of the cycle amplitudes of $H_2O + 2*CH_4$ (Figure 3c) to those of H_y (Figure 9) reveals that the increases in the cycle amplitudes above 5 hPa seen in $H_2O + 2*CH_4$ are consid-
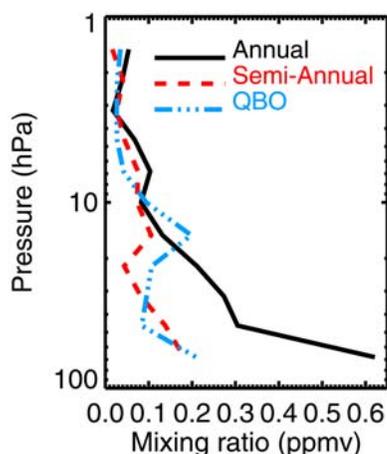
Figure 9. Profiles of annual (solid black line), semiannual (dashed red line), and QBO (dash-dotted blue line) cycle amplitudes from a least squares fit to HALOE H_y time series from 1996 to 2005 averaged over $10°S-10°N$. Below 5 hPa the cycle amplitudes are calculated from the $H_2O + 2*CH_4$ time series instead of H_y.

erably reduced in H_y. For instance, at 2.2 hPa, the QBO amplitude in H_y was reduced by 66% and the annual cycle amplitude was reduced by 52% relative to the respective amplitudes in the $H_2O + 2*CH_4$ time series. A general decrease in the cycle amplitudes with decreasing pressure is now observed over the entire stratosphere, with the exception near 15 hPa where the QBO winds and H_2O tape recorder signals interact to produce a local maximum in the QBO amplitude.

[47] If the time series of H_y has successfully removed the variations in $H_2O + 2*CH_4$ which are related to upper stratospheric chemistry, then the remaining variations result from variations in H_2O and CH_4 entering the stratosphere in the tropics. We can therefore use this time series along with CH_4 time series and the residual β values to calculate the time series of stratospheric entry H_2O mixing ratios. In order to obtain the entry H_2O from H_y, we subtract the H_2 mixing ratio and twice the CH_4 mixing ratio at 98 hPa. For CH_4 at the tropopause, the $2*CH_4$ mixing ratio between 1999 and 2005 (avoiding the immediate post-Pinatubo period) is 3.58 ppmv. For H_2 at the tropopause, a value of 0.55 ppmv is used [*Rohs et al.*, 2006]. If we use the 3.2 hPa H_y time series, we can derive the stratospheric entry H_2O result shown in Figure 10. Because it is based upon the 3.2 hPa time series, the calculated entry H_2O time series at 98 hPa is of course both smoothed and delayed by several years compared to the actual entry level time series. It should, however, be suitable for those interested in the average H_2O entry level values averaged over multiyear periods. For example, comparisons between the calculated entry H_2O time series and long-term records of balloon-borne midlatitude H_2O measurements in the lower stratosphere [*Oltmans et al.*, 2000; *Scherer et al.*, 2008] would be appropriate.

[48] The uncertainty in the stratospheric entry H_2O mixing ratio is driven by the errors in H_2O, $2*CH_4$, and $(\beta - 2)*d$ $\langle CH_4\rangle/dp$ in the H_y calculation. Since the HALOE data have been bias corrected to the ACE data, the H_2O and CH_4

systematic errors are effectively equal to those for ACE H_2O (5%) and CH_4 (10%) in the upper stratosphere. This 5% uncertainty in H_2O at 3.2 hPa introduces ~0.28 ppmv uncertainty in entry-level H_2O, while the 10% uncertainty in CH_4 introduces an uncertainty of ~0.18 ppmv. The error in β, estimated from the difference in the HALOE single-level β values between the 1:1 and 4:1 H_2O/CH_4 random error ratio cases for the monthly averaged data (see Table 2), is less than 0.1 at most pressures. The contribution of uncertainties in β to the total error in the entry H_2O mixing ratio is therefore ~0.02 ppmv. The total uncertainty in the entry H_2O mixing ratio from the above three error sources is calculated to be ~0.3 ppmv.

[49] Using the HALOE derived residual β values which minimized H_y variations at each level, we then investigated the vertical profile distributions of CH_4, $H_2O + 2*CH_4$, inferred H_2, and H_y in the equatorial upper stratosphere from HALOE, ACE, and MIPAS. Multiyear profiles of CH_4, $H_2O + 2*CH_4$, H_2, and H_y averaged over $10°S$ to $10°N$ for HALOE, ACE, and MIPAS data are shown in Figures 7b–7d. The mean profiles for HALOE and ACE are calculated by first taking multiyear monthly averages, then averaging the monthly averages. For MIPAS, a yearly average profile was calculated from monthly zonal mean data from October 2002 to September 2003. Results from MIPAS are similar using other 1 year periods. Yearly averages were calculated with all three data sets so as to remove potential seasonal cycle H_2O and CH_4 variations. The solid $H_2O + 2*CH_4$ profiles between 1.5 and 5 hPa do not show the typical near zero vertical gradient seen in the extratropical lower stratosphere [*Abbas et al.*, 1996; *Engel et al.*, 1996; *Hurst et al.*, 1999; *Nassar et al.*, 2005], but instead a slight positive value with mixing ratios increasing by about 0.4 ppmv over this range. We note that a previous study of MIPAS data [*Juckes*, 2007] has revealed this feature in $H_2O + 2*CH_4$. The inferred profiles of H_2 for each instrument are also shown (the third and fourth terms of equation (3)), which shows a ~0.3 ppmv reduction above 5 hPa. Mean profiles of H_y are calculated by summing the mean $H_2O + 2*CH_4$ and H_2 profiles. We note that the fifth term of equation (3) does not enter the calculation for H_y because the CH_4 residuals average to zero in the time mean. The H_y profiles generally show that the β values which minimize the time variation in H_y on individual levels also
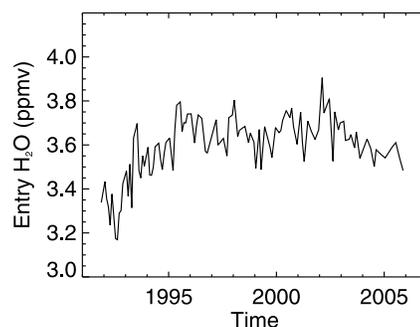

Figure 10. Time series of HALOE stratospheric entry water vapor at 98 hPa averaged over $10°S-10°N$ and derived from the HALOE H_y time series at 3.2 hPa. Note that this time series is both highly smoothed and delayed several years from the actual entry water vapor time series.
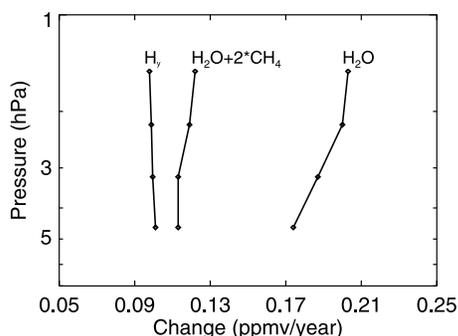
Figure 11. Vertical profiles of the change in H_2O, H_2O + $2*CH_4$, and H_y per year for 1992–1996 averaged over $10°S$–$10°N$. The yearly changes were calculated from a linear least squares fit to the HALOE time series which included QBO, annual, semiannual, and a linear trend term.

reduce the variation of total hydrogen with altitude. This is perhaps the most compelling evidence that the systematic adjustment which we have made to the HALOE data based on comparisons with ACE is reasonable.

[50] The general altitude dependence of the mean H_2O + $2*CH_4$ and H_2 profiles is similar between the CHEM2D results (Figure 7a) and the observations (Figures 7b–7d), though the vertical gradients are about half as large for the model. As mentioned earlier, we suspect that discrepancies between the modeled and actual atmospheric circulation could contribute to these differences. Indeed, a slight difference in circulation between the model and observations is supported by the slightly larger drop in CH_4 with altitude in the CHEM2D model relative to the CH_4 measurements shown in Figure 7.

[51] An interesting ramification of the H_y calculation is that the increase observed in H_2O + $2*CH_4$ during the early and middle 1990s [e.g., *Nedoluha et al.*, 2003] is slightly reduced in magnitude. We analyze the yearly changes by performing least squares fits to the H_2O, H_2O + $2*CH_4$, and H_y time series over the 1992–1996 time period where we have included a linear trend term to the fit in addition to QBO, annual, and semiannual terms. The yearly changes for each parameter are derived from the linear fit term, which is plotted at 4 pressure levels (Figure 11). This shows that at 3.2 hPa about 40% of the total change in H_2O is attributable to changes in CH_4, and ~12% of the remaining variation is attributable to changes in H_2. The 1 sigma uncertainties as calculated from the trend term in the fits are, at 2.2 hPa, ~0.03 ppmv/yr for H_2O, ~0.02 ppmv/yr for CH_4, and ~0.01 ppmv/yr for H_y. The trends are highly correlated over these levels, so, while these uncertainties are larger than the level-to-level differences, the altitude dependence may nevertheless be significant. Figure 11 reveals an altitude dependence in the yearly changes for H_2O. Most, but not all, of this altitude dependence is removed in H_2O + $2*CH_4$, and the altitude dependence is further reduced in the H_y profile. The H_y change profile is physically reasonable since it implies that the change in entry level H_2O is affecting all levels in the equatorial upper stratosphere nearly equally, but with a very slightly smaller increase at the highest level. The similarity of H_y changes throughout the upper stratosphere is plausible given the short time scale of circulation in the upper stratosphere of ~1 year [*Hall and*

Waugh, 1997] (compared with the 1992–1996 time period) and the near linearity of the early and middle 1990s H_y "trends" (see Figure 8).

[52] The early to middle 2000s time period was examined to investigate possible changes in H_2O in the equatorial upper stratosphere given the documented drying of the equatorial lower stratosphere in 2001 [*Randel et al.*, 2006]. A similar analysis to that performed for the early 1990s was done for this time period, but the upper stratospheric changes in H_2O, H_2O + $2*CH_4$, and H_y were much smaller than in the early 1990s and no clear conclusions could be drawn for this period.

7. Discussion and Conclusions

[53] We have presented data from the HALOE, ACE, and MIPAS instruments which reflect the nonconservation of H_2O + $2*CH_4$ on individual pressure surfaces over time or as a time-averaged quantity as a function of pressure in the equatorial upper stratosphere. Several plausible mechanisms were investigated to explain the variations in H_2O + $2*CH_4$ such as systematic data biases and vertical resolution differences in the HALOE H_2O and CH_4 data. The impacts of these mechanisms were found to be too small to account for the size of the H_2O + $2*CH_4$ changes.

[54] The equatorial upper stratosphere is the ideal region to calculate β values since the CH_4 changes are large, the descent of air from higher altitudes is small, and influence of variations in stratospheric entry level H_2O is much smaller than in the lower stratosphere. After applying bias corrections to HALOE and MIPAS H_2O and CH_4 profiles, β values calculated from the HALOE, ACE, and MIPAS showed good agreement both on single pressure surfaces and over a range of pressures in the equatorial upper stratosphere with values considerably above 2. We calculated values of β which minimized the variability of H_y, or total hydrogen, time series on individual pressure surfaces. The smoother H_y time series (compared with the H_2O + $2*CH_4$ time series) was then used to derive a time series of stratospheric entry level H_2O near the tropopause. The calculation of the stratospheric entry H_2O mixing ratio based on H_y in the tropical upper stratosphere provides a more appropriate value compared to one based on H_2O + $2*CH_4$ due to the necessity in accounting for the net reduction in H_2 between the tropopause and the upper stratosphere at tropical latitudes.

[55] The measurements are supported by atmospheric simulations by the CHEM2D model which show not only variations in H_2O + $2*CH_4$ in the upper stratosphere but also variations in H_2 of similar magnitude but anticorrelated in time so that H_2O + $2*CH_4$ + H_2 is nearly conserved. Theoretical analysis by *Le Texier et al.* [1988] has shown that oxidation of H_2 plays a key role in the H_2O budget of the stratosphere. *Le Texier et al.* [1988] showed that, between 40 and 50 km, there was net loss of H_2 which drives additional H_2O production thus producing positive vertical gradients in H_2O + $2*CH_4$. This behavior is what is seen in the HALOE, ACE, and MIPAS profiles of H_2O + $2*CH_4$ and inferred H_2 in the upper stratosphere, where CH_4 oxidation occurs most efficiently. The amount of the excess H_2O + $2*CH_4$ above 5 hPa is ~0.4 ppmv, which is

nearly offset by a ~ 0.3 ppmv net reduction of H_2 (see Figure 7).

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