The Hydrogen Budget of the Stratosphere Inferred from ATMOS Measurements of H₂O and CH₄

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Abstract. The total hydrogen budget of the stratosphere and lower mesosphere has been examined using vertical mixing ratio profiles of H₂O and CH₄ measured by the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment from four Space Shuttle missions. The oxidation of CH₄ and H₂ is investigated by evaluating the quantity \( \frac{dH}{dt} = \frac{H_2O + 2CH_4}{entering\,the\,stratosphere} \) and examining its conservation with altitude in the upper atmosphere. Data from all four ATMOS missions indicate H₂ to be nearly conserved in the lower stratosphere and to exhibit a broad maximum in the 35-65 km range. The observations provide evidence of a secondary source of H₂O from H₂ oxidation at altitudes from 35 to 55 km, and net production of H₂ at altitudes above 55 km. ATMOS measurements of H₂O and CH₄ permit the first evaluation of a sickle-shaped distribution of H₂ which is qualitatively consistent with profiles calculated using 2-dimensional models.

Introduction

Stratospheric and lower mesospheric hydrogen resides mostly in H₂O, CH₄, and H₂ with negligible contributions to the total budget expected from all other constituents. In the lower stratosphere, the oxidation of CH₄ produces approximately two molecules of H₂O for each molecule of CH₄ that is removed, and the gradient \( \frac{dH_2O}{dCH_4} \) is expected to be nearly equal to -2. Production of H₂ from oxidation of CH₄ is nearly balanced by production of H₂, so that the mixing ratio of H₂ remains nearly constant with altitude in the lower stratosphere. \( H_2O \) measurements of H₂O to date have been acquired by rockets or from balloons using grab sampling techniques and are limited to altitudes below -40 km (e.g., Ehhalt and Tonnisen, 1980; Schmidt et al., 1974; Fabian et al., 1979).

\( 0|1 + H_2O \rightarrow H_2O + O_2 \) (1)

and constitute the main photochemical source of water vapor in the stratosphere. Water vapor is lost in the stratosphere by

\( 1|20 + O(1D) \rightarrow 20|1 \),

and in the mesosphere by photolysis

\( H_2O \rightarrow H + OH \). 3)

H₂ is produced by

\( \text{CH}_3\text{O} + \text{hv} \rightarrow \text{H} + \text{CH}_2\text{O} \) (4)

and is lost by oxidation due to \( O(1D) \), similar to methane,

\( \text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \) (6)

\( \text{H}_2\text{O} + \text{hv} \rightarrow \text{H} + \text{H}_2 + 0(1) \) (7)

Calculations indicate that the major source (80-95%) of H₂ in the stratosphere, and the lower mesosphere up to altitudes of -55 km is the photolysis of \( \text{CH}_3\text{O} \) (Eq. 4) with a minor contribution from reaction (5) (e.g., Brasseur and Solomon, 1986). In the mesosphere at altitudes above 55 km, \( \text{H}_2 + \text{H}_2\text{O} \) and the photolysis of \( \text{H}_2\text{O} \) (Eqs. 6 and 7) dominate the production of \( \text{H}_2 \). Loss of 11,
in the stratosphere occurs by reaction with 011 (Hq. 8) while loss in the mesosphere is dominated by reaction with O(1D)(Hq. 9). The three species CH4, H2O, and H2 are rather long lived in the lower stratosphere with similar photochemical lifetimes of many years; lifetimes decrease to only a few months at 40 km, in the upper stratosphere and lower mesosphere, the lifetime of H2 increases progressively back to a few years. The time constants for transport for the three species are comparable to the photochemical lifetimes (e.g., Le Texier et al., 1988); consequently, the effect of transport processes are significant in determining global distributions.

Water Vapor and Methane Distributions

I high-resolution infrared limb viewing solar occultation observations by ATMOS have been carried out on four shuttle missions starting with Spacelab 3 in April 1985, and ATLAS 1 to 3 in April 1992, October 1993, and November 1994, respectively. Data from each mission has been processed in a similar manner using ATMOS Version 2 processing algorithms (Gunson et al., 1996). These observations provide simultaneous measurements of mixing ratio profiles of H2O and CH4 over various latitudes, employing optical bandpass filters in the 1100-2000 cm\(^{-1}\), 650-2450 cm\(^{-1}\), and 1580-3420 cm\(^{-1}\) spectral regions. ATMOS retrieves mixing ratios of H2O and CH4 with estimated total uncertainties of ~6% and 5%, respectively (Gunson et al., 1996).

A comparison of ATMOS observations of H2O, CH4, and N 0 with nearly coincident in situ measurements obtained in the lower stratosphere during November 1994 demonstrates the high degree of accuracy and precision of the space-borne observations (Chang et al., 1996). The current analyses examine the H2O and CH4 measurements obtained from the four ATMOS missions, with a particular emphasis on the comprehensive data provided by the ATLAS-3 mission obtained over the 8 to 49°N latitude range. The high accuracy and precision of these measurements permits a qualitative evaluation of the total hydrogen budget of the upper atmosphere.

Figure 1 shows correlation plots of H2O vs CH4 for all four ATMOS missions, restricted to data obtained out of the polar vortex regions, with the open circles indicating data obtained in the 18-35 km range and the crosses representing data outside this range. The dotted lines in Fig. 1 with fixed slopes of -2 represent expected distributions if oxidation of each CH4 molecule were to produce 2 molecules of H2O. Deviations of the data from a slope of -2 provide information about the total hydrogen budget of the stratosphere. The solid lines in Fig. 1 show a linear least square fit to all measurements obtained at altitudes of 28 and 35 km. This altitude region was chosen to restrict our analysis to stratospheric air, for regions where the mixing ratio of H2 is not expected to vary appreciably (e.g., Le Texier et al., 1988).

The slope of the linear fit in Fig. 1 arc -2.28 ± 0.14 for Spacelab 3, and -2.12 ± 0.07, -2.13 ± 0.14, and 2.00 ± 0.04 for ATLAS 1 to 3 missions, respectively, with the uncertainties indicating the 1σ standard deviation of the linear regression. The estimated total uncertainties in the slope, accounting for the total uncertainty in the measurements of H2O and CH4 arc ± 0.23 for Spacelab 3, and ± 0.18, 0.21, and 0.16 for ATLAS 1 to 3, respectively. The weighted mean slope \( \delta\text{H}_2\text{O}/\delta\text{CH}_4 = -2.07 ± 0.16 \) for the four ATMOS missions indicates near conservation of total H in the lower and middle stratosphere. The region above Cl 1.4-0.8 ppmv, however, exhibits excess H2O and more negative slope for all four missions, and will be discussed further in the next section.

The intercepts of the linear least square fits represent the average total hydrogen in the 18 to 35 km region: 6.96 ± 0.15 ppmv for Spacelab 3, and 7.02 ± 0.07, 7.22 ± 0.14, and 7.21 ± 0.04 ppmv for ATLAS 1 to 3, respectively, with the uncertainties indicating the 1σ standard deviation of the linear regression. With estimated systematic errors of 6% for H2O and 5% for CH4, the total uncertainties in the intercept are calculated to be ± 0.44 ppmv for Spacelab 3, and ± 0.43, 0.45, and 0.43 ppmv for ATLAS 1 to 3, respectively. Our estimate, for the amount of H2O entering the stratosphere, is based on linear least square fits to ATMOS measurements of H2O and CH4 collected over a wide range of altitudes and latitudes, rather than actual observations at the tropopause, to minimize the sensitivity of our results to seasonal variations on H2O. Seasonal oscillations present in individual ATMOS occultations are likely to be averaged out by this process, since air with a variety of ages is examined (Dessler et al., 1994). Using a CH4 mixing ratio of 1.70 ppmv for 1994 at the tropopause, and assuming an average yearly CH4 increase of 0.46%/year between 1990 and 1994 and a 0.73%/year increase over the period 1985 to 1989 (WMO, 1994), we deduce the H2O content of air entering the stratosphere for the four missions to be: 3.28 ± 0.31 ppmv for Spacelab 3, and 3.45 ± 0.28, 3.62 ± 0.31, and 3.81 ± 0.29 ppmv for ATLAS 1 to 3, respectively. A mean value of 3.65 ± 0.28 ppmv of H2O entry into the stratosphere, weighted to the number of observed occultations, is thus inferred from the database of the four ATMOS missions.

The mean value of H2O entering the stratosphere observed by ATMOS is systematically lower, but within the uncertainty of measurement, than the value 4.2 ± 0.5 ppmv obtained by in situ measurements during May 1993 (Dessler et al., 1994). A more detailed comparison of the hydrogen budget inferred by ATMOS with analyses based on other remote and in situ measurements is given in Abbas et al. (1996), which focuses on the seasonal variation of H2O in the tropical lower stratosphere observed by ATMOS. The lower stratosphere observed by ATMOS during the Spacelab 3 mission in April 1985 appears dry relative to the later ATMOS measurements. It is unclear what significance, if any, to attach to the apparent trend in the H2O content of air entering the stratosphere inferred from the four missions, which is considerably larger than a 0.8 % per year trend in stratospheric H2O that has been inferred from a ten-year time series of frost-point hygrometer measurements at Boulder, CO (Oltmans and Hofmann, 1995). A more comprehensive analysis to address the significance of the apparent trend should account fully for the different latitudinal and seasonal coverage of the four missions, possible biases associated with the ATMOS retrievals of H2O using its various optical filters, as well as an examination of satellite, balloon-borne, and in situ measurements of CH4 and H2O over the past decade.

Hydrogen Budget of the Stratosphere and Lower Mesosphere

Simultaneous measurements of H2O and CH4 provided by ATMOS permit an evaluation of the partitioning of hydrogen species in the stratosphere and lower mesosphere. The
correlation plots (Fig. 1) for all four missions indicate an excess of \( H_2O \) relative to the amount supplied by oxidation of \( CH_4 \) for \( CH_4 \) less than -0.5 ppmv (corresponding to altitudes of -35 km). The excess \( H_2O \) present in this region of the correlation plots is evidence of a source of 1120 from oxidation of \( H_2 \). For \( CH_4 \) mixing ratios less than -0.2 ppmv (altitudes of ~ 50 km), \( H_2O \) and \( CH_4 \) are positively correlated, demonstrating the conversion of \( H_2O \) and \( CH_4 \) to \( H_2 \) by reactions \( H + H_2O \) and photolysis of \( H_2O \) (Figs. 6 and 7).

A vertical distribution for \( H_2 \) can be inferred from ATMOS measurements of \( H_2O \) and \( CH_4 \) by assuming total hydrogen \( H = (H + H_2) \) transported to the lower stratosphere from the troposphere is conserved with altitude. Figures 2a-b show the average vertical profiles of \( CH_4 \), \( H_2O \), and \( H \) obtained from 27 ATMOS/ATLAS-3 representative sunset occultations for mid-latitudes in the 28-49°N range, and from 13 occultations for low-\( \lambda \) altitudes in the 8-28°N range, respectively. The error bars indicate the quadrature sum of 10 standard deviation of the mean values and systematic errors arising from 6% and 5% uncertainties in the spectral parameters of \( H_2O \) and \( CH_4 \). The vertical profiles of \( H \) have been smoothed using polynomial curves to remove small scale structures. It is clear from both the observed and smoothed plots that \( H \) is conserved with altitude. The maximum of the quantity \( H \) at altitudes higher than 60 km demonstrates that production of \( H_2 \) by \( H + H_2O \) and photolysis of \( H_2O \) become important at these altitudes.

Distributions of \( H_2 \) have been derived by subtracting the smoothed curve for \( H \) from a constant value for \( H_2 \) of 7.80 ppmv assuming a tropospheric mixing ratio of \( H_2 = 0.55 \) ppmv (Ihhal and Tonnissen, 1980) and a value of \( H = 7.25 \) ppmv based on ATMOS/ATLAS-3 observations in the N1 1 at mid-\( \lambda \) latitudes and the tropics. The minimum mixing ratio inferred for \( H_2 \) at mid-latitudes is \( 0.15 \pm 0.1 \) ppmv at -50 km, and 0.18 \( \pm 0.1 \) ppmv at the tropics. The uncertainty in this case represents the standard deviation of the mean profile for \( H \) and does not include systematic errors in the measurements of \( H_2O \) and \( CH_4 \). The inferred profile for \( H_2 \) is sensitive also to seasonal and episodic variations in \( H \), neither of which are accounted for in the present analysis. For example, profiles for \( H_2 \) inferred from \( H + H_2O \) measurements (not shown) exhibit a shallower minimum (less variation with altitude) than profiles shown in Fig. 2.

A comparison of the plots in Figs. 2a-b shows that the mixing ratios of \( H_2O \) are higher and of \( CH_4 \) are lower at the mid-latitudes for altitudes below -50 km, as expected from the Brewer circulation. Consistent with the indicated latitudinal differences in \( H_2O \) and \( CH_4 \) distributions, the inferred \( H_2 \) mixing ratios are higher in the mid-\( \lambda \) latitude stratosphere below 50 km, where \( CH_4 \) mixing ratios are higher and \( H_2 \) is produced by oxidation of \( CH_4 \) via \( CH_4 + H \) in the mesosphere above 50 km, \( H_2 \) produced by \( H + H_2O \) and photolysis of \( H_2O \) leads to higher values in the tropics compared with the mid-latitudes.

Fig. 2c shows a comparison of the inferred \( H_2 \) distributions with the profiles for mid-latitudes and the tropics calculated by Le Texier et al. (1988) using a 2-dimensional model with coupled photochemistry and dynamics. Also shown by open circles are the observed values of \( H_2 \) limited to 35 km altitude, at 32°N (Ihhal and Tonnissen, 1980). Although the inferred 112 distributions for mid-latitudes appear to be qualitatively similar to the model calculations, the minimum inferred values are lower than the model values. The altitude of minimum \( H_2 \), however, appears to be in general agreement with the 2-dimensional model.

It should be noted that in the inferred 112 distributions ignore the effects of transport from the mesosphere to the stratosphere. Model calculations by Le Texier et al., however, indicate that mesospheric transport effects are important for high latitudes in the winter where air rich in \( H_2 \) is transported to lower altitudes in the stratosphere. Since such large values of \( H_2 \) have not been inferred for the low and mid-\( \lambda \) altitudes regions considered here, consistent with the model calculations of Le Texier et al., the effect of mesospheric transport does not appear to be evident.

Conclusions

An examination of measurements of \( H_2O \) and \( CH_4 \) made by ATMOS indicates that the quantity \( H = (H_2O + 2CH_4) \) is conserved in the lower and middle stratosphere and yields an average water vapor entry into the stratosphere of 3.66 \( \pm 0.28 \) ppmv. \( H \) is not conserved in the upper stratosphere and lower mesosphere and has a curved structure with a maximum at -50-55 km. This structure is evident in the correlation plots of \( H_2O \) vs \( CH_4 \) for all four missions. The region near -50 km is characterized by an excess abundance of \( H_2O \) - 0.4 ppmv, providing evidence of a source of \( H_2O \) from oxidation of \( CH_4 \), whereas the decrease in \( H \) observed at higher altitudes implies net production of \( H_2 \) from \( H_2O \) and \( CH_4 \) The distribution of \( H_2 \) inferred from variation of \( H \) with altitude indicates a sickle-shaped profile with a constant mixing ratio at altitudes of \( \leq 35 \) km, a minimum at -50 km, and increasing to > 1 ppmv above 65 km. The inferred distribution of \( H_2 \) is in qualitative agreement with the values obtained from a 2-dimensional coupled photochemical-dynamical model.

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References


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Figure 1. (a) Plot of H$_2$O vs CH$_4$ for 8 occultations for Spacelab-3 (April, 1985) over 50°S-31°N latitudes (b) Same for 50 occultations for ATLAS-1 (March, 1992) over 54°S-28°N latitudes (c) Same for 26 occultations of ATLAS-2 (October, 1993) over 50°S-67°N latitudes (d) Same for 88 occultations of ATLAS-3 (November, 1994) in the 72°S-54°N latitude range. Data obtained at altitudes between 18 and 35 km are indicated by open circles, crosses represent data obtained outside this range. Only data obtained outside polar vortices are shown. The solid lines represent linear least square fits to the data in the 18-35 km range (equations given in the text), and the dotted lines represent fits to the same data of lines with a fixed slope of -2.

Figure 2: (a) The vertical profiles of CH$_4$, H$_2$O, and H$=(H_2O + 2CH_4)$ from a zonal average of 33 sunset occultations over 31-49°N. The solid line shows a curve-fit for H with a linear-fit in the lower region (b) Same as in (a) for 14 occultations over 8-28°N (c) Comparison of inferred H$_2$ distributions for mid- (filled circles) and low-latitudes (diamonds) with 2-dimensional model calculations of LeTexier et al. (1988). Observed values of H$_2$ for 32°N are shown in open circles (Ihnhalt and Toonissen, 1980)
$CH_4$ mixing ratio (ppmv)

$H_2O$ mixing ratio (ppmv)

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X Outside 18-35 km  O Inside 18-35 km — Fitted to data — Slope set equal to -2

ATLAS3 $H_2O = (7.21382\times10^{-6} \pm 4.08748\times10^{-8}) - (1.99952 \pm 0.036119) \times CH_4$

ATLAS2 $H_2O = (7.21953\times10^{-6} \pm 1.36857\times10^{-7}) - (2.13339 \pm 0.137212) \times CH_4$

ATLAS1 $H_2O = (7.02218\times10^{-6} \pm 7.40953\times10^{-8}) - (2.12456 \pm 0.067653) \times CH_4$

Splab3 $H_2O = (6.95644\times10^{-6} \pm 1.45546\times10^{-7}) - (2.28001 \pm 0.142649) \times CH_4$

Errors are 10 random