The Hydrogen Budget of the Stratosphere Inferred from ATMOS Measurements of H_2O and CH_4

M. M. Abbas[1], M. R. Gunson[2], M. J. Newchurch[3], H. A. Michelsen[4], R. J. Salawitch[2], M. Allen[5], M. C. Abrams[6], A.. Y. Chang[2], A. Goldman[7], F. W. Irion[5], E. J. Moyer[5], R. Nagaraju[3], C. P. Rinsland[6], G. P. Stiller[8], and R. Zander[9]

Abstract. The total hydrogen budget of the stratosphere and lower mesosphere has been examined using vertical mixing ratio profile.s of H_2O and CH_4 measured by the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment from four Space Shuttle missions. The oxidation of CH_4 and H_2 is investigated by evaluating the quantity $\boldsymbol{H}$ (= H_2O + $2CH_4$) entering the stratosphere, and examining its conservation with altitude in the upper atmosphere. Data from all four ATMOS missions indicate $\boldsymbol{H}$ 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 H_2O from H_2 oxidation at altitudes from 35 to 55 km, and net production of H_2 at altitudes above - 55 km. ATMOS measurements of H_2O and CH_4 permit the first evaluation of a sickle-shaped distribution of H_2 which is qualitatively consistent with profiles calculated using 2-dimensional models.

Introduction

Stratospheric and lower mesospheric hydrogen resides mostly in H_2O, CH_4, and H_2 with negligible contributions to the total budget expected from all other constituents. In the lower stratosphere, the oxidation of CH_4 produces approximately two molecules of H_2O for each molecule of CH_4 that is removed, and the gradient $\partial H_2O / \partial CH_4$ is expected to be nearly equal to -2, Production of H_2 from oxidation of CH_4 is nearly balanced by oxidation of H_2, so that the mixing ratio of H_2 remains nearly constant with altitude in the lower stratosphere. Model calculations (Le Texier et al., 1988) suggest the mixing ratio of H_2 reaches a broad minimum in the mid-stratosphere, where oxidation begins to proceed more rapidly, and increases at higher altitudes due to production from photolysis of H_2O. The few measurements of stratospheric H_2 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).

[1] NASA Marshall Space Flight Center
[2] Jet Propulsion Laboratory, California Institute of Technology
[3] University of Alabama at Huntsville
[4] Harvard University
[5] California Institute of Technology
[6] SAIC - NASA Langley Research Center
[7] Denver University
[8] Forschungszentrum Karlsruhe/Universitact Karlsruhe
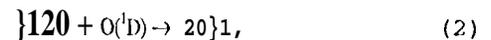[9] Institute of Astrophysics, University of Liege

In this paper, vertical profiles of H_2O and CH_4 measured by ATMOS are examined to evaluate the hydrogen budget of the stratosphere and lower mesosphere. The conservation of hydrogen between H_2O and CH_4 is examined for different altitude regions. The distribution of H_2 is inferred by calculating the average H_{tot} entering the lower stratosphere, and requiring the total hydrogen $H_{tot} = \boldsymbol{H} + H_2$ to be conserved with altitude.

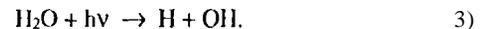## Photochemistry of Stratospheric Hydrogen Compounds

The distribution of H_2O in the stratosphere is maintained by oxidation of CH_4 by reaction with OH, $O(^1D)$, and to a lesser extent Cl, producing formaldehyde (CH_2O) with a chain of reactions (e.g., Rates and Nicolet, 196S; Ehhalt and Tonnisen, 1980; Brasseur and Solomon, 1986). Formaldehyde is converted into H_2, CO, and H_2O by photolysis and reaction with OH. The end products of the above chain of reactions are hydrogen radicals (H, OH, and HO_2) with lifetimes of less than a day, which quickly recombine to form H_2O mainly with the reaction
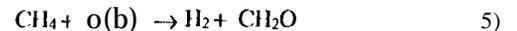
$$OH + HO_2 \rightarrow H_2O + O_2 \tag{1}$$
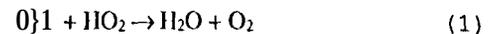
and constitute the main photochemical source of water vapor in the stratosphere. Water vapor is lost in the stratosphere by

$$H_2O + O(^1D) \rightarrow 2OH, \tag{2}$$
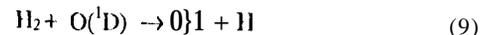
and in the mesosphere by photolysis

$$H_2O + h\nu \rightarrow H + OH. \tag{3}$$

H_2 is produced by

$$CH_2O + h\nu \rightarrow H_2 + CO \tag{4}$$

$$CH_4 + O(^1D) \rightarrow H_2 + CH_2O \tag{5}$$

$$H + HO_2 \rightarrow H_2 + O_2 \tag{6}$$

$$H_2O + h\nu \rightarrow H_2 + O(^1D) \tag{7}$$

and is lost by oxidation due to OH and $O(^1D)$, similar to methane,

$$H_2 + OH \rightarrow H_2O + H \tag{8}$$

$$H_2 + O(^1D) \rightarrow OH + H \tag{9}$$

Calculations indicate that the major source (80-95%) of H_2 in the stratosphere. and the lower mesosphere up to altitudes of -55 km is the photolysis of CH_2O (Eq. 4) with a minor contribution from reaction (5) (e.g., Brasseur and Solomon, 1986). In the mesosphere at altitudes above 55 km, $H + HO_2$ and the photolysis of H_2O (Eqs. 6 and 7) dominate the production of H_2. Loss of H_2

in the stratosphere occurs by reaction with OH (Eq. 8) while loss in the mesosphere is dominated by reaction with $O(^1D)$ (Eq. 9). The three species CH_4, H_2O, and Hz ate 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 H_2 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

1 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 H_2O and CH_4 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 H_2O and CH_4 with estimated total uncertainties of ~ 6% and 5%, respectively (Gunson et al., 1996). A comparison of ATMOS observations of H_2O, CH_4, and N_2O 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 H_2O and CH_4 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 H_2O vs CH_4 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 CH_4 molecule were to produce 2 molecules of H_2O. 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 between altitudes of 18 and 35 km. This altitude region was chosen to restrict our analysis to stratospheric air, for regions where the mixing ratio of H_2 is not expected to vary appreciably (e.g., Le Texier et al., 1988).

The slopes of the linear fits in Fig. 1 are -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 H_2O and CH_4, are: ± 0.23 for Spacelab 3, and ± 0.18, 0.21, and 0.16 for ATLAS 1 to 3, respectively. The weighted mean slope $\partial H_2O / \partial CH_4$ = -2.07 ± 0.16 for the four ATMOS missions indicates near conservation of total H in the lower and middle stratosphere. The

region above CI 1.4- 0.8 ppmv, however, exhibits excess H_2O 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 f/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 pprnv 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 H_2O and 5% for CH_4, 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 H_2O entering the stratosphere. is based on linear least square fits to ATMOS measurements of H_2O and CH_4 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 H_2O. 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 CH_4 mixing ratio of 1.70 ppmv for 1994 at the tropopause, and assuming an average yearly CH_4 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 H_2O 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 H_2O 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 H_2O entering the stratosphere observed by ATMOS is systematically lower, but within the uncertainty of measurement, than the value 4.2 ± 0.5 ppm 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 H_2O 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 H_2O content of air entering the stratosphere inferred from the four missions, which is considerably larger than a 0.8 % per year trend in stratospheric H_2O 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 H_2O using its various optical filters, as well as an examination of satellite, balloon-borne, and in situ measurements of CH_4 and H_2O over the past decade.

Hydrogen Budget of the Stratosphere and Lower Mesosphere

Simultaneous measurements of H_2O and CH_4 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 H_2O from oxidation of H_2. For CH_4 mixing ratios less than ~ 0.2 ppmv (altitudes of ~ 50 km), H_2O and CH_4 arc positively correlated, demonstrating the conversion of H_2O and CH_4 to H_2 by reactions $H + HO_2$ and photolysis of H_2O (Eqs. 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 $H_{tot} = (H$ -t $H_2)$ 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 ATLAS-3 representative sunset occultations for mid-latitudes in the 28-49°N range, and from 13 occultations for low-] 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 not conserved with altitude. The maximum of the quantity H at altitudes higher than 60 km demonstrates that production of' 112 by $H + H_2O_2$ and photolysis of H_2O become important at these altitudes.

Distributions of H_2 have been derived by subtracting the smoothed curve lit for H from a constant value for H_{tot} of 7.80 ppmv assuming a tropospheric mixing ratio of $H_2 = 0.55$ ppmv (Ehhalt and Tonnisen, 1980) and a value of $H = 7.25$ ppmv based on ATMOS/ATLAS-3 observations in the N} I at mid-] latitudes and the tropics. The minimum mixing ratio inferred for H_2 at mid-latitudes is 0.15 ± 0.1 ppmv at - 50 km, and $0,18 \pm 0.1$ pprnv at the tropics. The uncertainty in this case represents the standard deviation of the mean profile for H, and dots 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 arc accounted for in the present analysis. For example, profiles for H_2 inferred from ATLAS 1 measurements (not shown) exhibit a shallower minimum (less variation with altitude) than profiles shown in Fig. 2.

A comparison of the plots in Pigs. 2a-b shows that the mixing ratios of H_2O arc higher and of CH_4 arc 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 arc higher in the mid-] altitude stratosphere below 50 km 'where CH_4 mixing ratios arc higher and H_2 is produced by oxidation of CH_4 via CH_2O. In the mesosphere above 50 km, H_2 produced by } 1 + HO_2 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 arc the observed values of H_2 limited to 35 km altitude, at 32°N (Ehhalt and Tonnisen, 1980). Although the inferred 112 distributions for rnid-latitudes appear to be qualitatively similar to the model calculations, the minimum inferred values arc lower than the model values. The altitude of minimum }12, however,

appears to be in general agreement with the 2-dimensional model. It should be noted that the in ferred 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 arc 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-] altitudes regions considered here, consistent with the model calculations of Le Texier et al., the effect of mesospheric transport docs 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 H_2, 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 ≤ 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.

References

Abbas, et al., Stratospheric measurements of water vapor and methane by ATMOS/ATLAS-3: Methane oxidation and troposphere to stratosphere transport, Geophys. Res. Lett., this issue, 1996.

Bates, D. R. and M. Nicolet, Atmospheric hydrogen, Plan. Spa, Sci., 13, 905-909, 1965.

Brasseur, G. and S. Solomon, Aeronomy of the Middle Atmosphere, D. Reidel Publishing, Holland, 19S6.

Dessler, A. E., et al., An examination of the total hydrogen budget of the lower stratosphere, 21, 2563-2566, 1994.

Ehhalt, D. }1. and A. Tonnisen, Hydrogen and carbon compound in the stratosphere, 129-151, in Proc. NATO Advan. Study Institute on Atmospheric Ozone, eels., M. Nicolet and A. C. Aiken, U. S. Department of Transportation, Washington, D. C., 1980.

Fabian, P., et al., Simultaneously measured vertical profiles of H_2, CH_4, CO, N_2O, $CFCl_3$, and CF_2Cl_2 in the midlatitude stratosphere and troposphere, J. Geophys. Res., 84, 3149, 1979.

Gunson, M. R,, et al., The Atmospheric 'f'race Molecule Spectroscopy experiment deployment on the ATLAS-3 Space Shuttle Mission, this issue.

Le Texier, H.S. Solomon, and R.R. Garcia, The role of molecular hydrogen and methane oxidation in the water vapor budget of the stratosphere, Q.J.R. meteorol, Sot., 114, 281-295, 1988.

Oltmans, S. J., and D. J. Hofmann, Increase in lower-sirsrtcrspheric water vapor at a mid-latitude northern hemisphere site from 1981 to 1994, Nature, 374, 146-149, 1995.

Schmidt, U., Molecular hydrogen in the atmosphere, Tellus, 26, 78. 1974.

Figure 1. (a) Plot of H_2O 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 tits to the same data of lines with a fixed slope of -2.
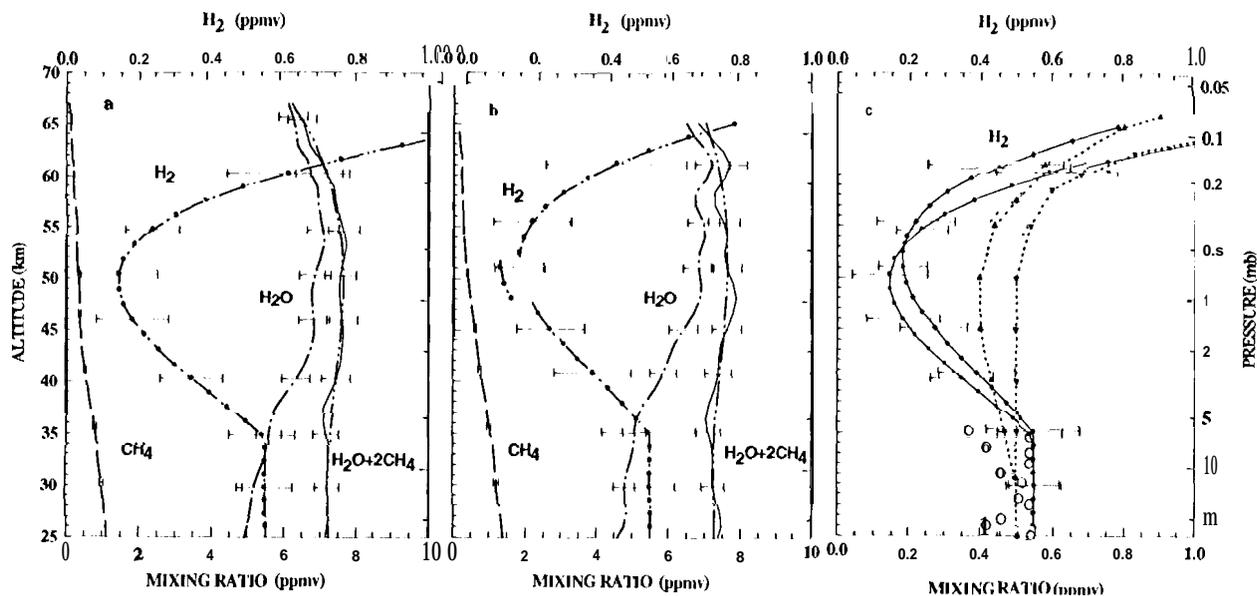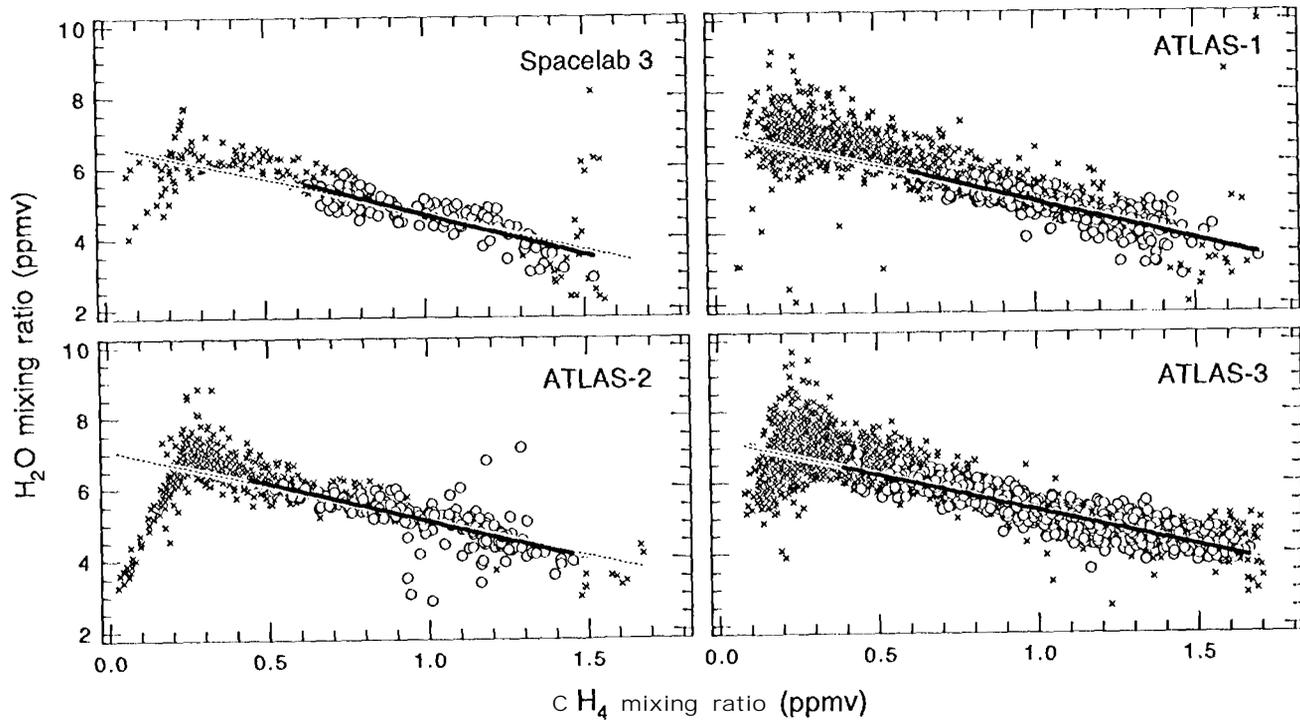

Figure 2: (a) The vertical profiles of CH_4, H_2O, and $H = (H_2O + 2CH_4)$ from a zonal average of 33 sunset occultations over 31-$49°N$. The solid line shows a curve-fit for H, with a linear-fit in the lower region (b) Same as in (a) for 14 occultations over 8-$28°N$ (c) Comparison of inferred H_2 distributions for mid- (filled circles) and low-latitudes (diamonds) with 2-dimensional model calculations of Le Texier et al. (1988). Observed values of H_2 for $32°N$ are shown in open circles (Ehhalt and Tonnisen, 1980)

Figure shows four scatter plots of H_2O mixing ratio (ppmv) versus $c\,H_4$ mixing ratio (ppmv) for Spacelab 3, ATLAS-1, ATLAS-2, and ATLAS-3.

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

ATLAS3 $H2O = (7.21382\text{e-}06 \pm 4.08748\,\text{e-}08) - (1.99952 \pm 0.036119)\,CH4$
ATLAS2 $H2O = (7.21953\text{e-}06 \pm 1.36857\text{e-}07) - (2.13339 * 0.137212)\,CH4$
ATLAS1 $H2O = (7.02218\text{e-}06 \pm 7.40953\text{e-}08) - (2.12456 * 0.067653)\,CH4$
Splab3 $H2O = (6.95644\text{e-}06 \pm 1.45546\text{e-}07) - (2.28001 \pm 0.142649)\,CH4$

Errors are 1σ random