The hydrogen isotopic composition of water vapor entering the stratosphere inferred from high-precision measurements of δD-CH$_4$ and δD-H$_2$

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[1]   The hydrogen isotopic composition of water vapor entering the stratosphere provides an important constraint on the mechanisms for dehydration of air ascending through the tropical tropopause layer. We have inferred the annual mean hydrogen isotopic composition of water vapor entering the stratosphere (or δD-H$_2$O$_0$) for the mid to late 1990s based on high-precision measurements of the hydrogen isotopic compositions of stratospheric H$_2$ and CH$_4$ from whole air samples collected on the NASA ER-2 aircraft between 1996 and 2000 and remote observations of δD-H$_2$O from the FIRS-2 far infrared spectrometer. We calculate an annual mean value for δD-H$_2$O$_0$ of -653 ($+24/-25$)‰ relative to Vienna standard mean ocean water (VSMOW). Previous inferences from balloon-borne and spacecraft remote-sensing observations are ~20‰ lighter than the value from this analysis. We attribute the difference to an underestimation of deuterium in the molecular H$_2$ reservoir in earlier work. This precise and more accurate value for the annual mean δD-H$_2$O$_0$ will be useful as a 1990's benchmark for detecting future changes in the details of the dehydration of air due to the impact of climate change on convection intensity, cloud microphysics, or tropical tropopause layer temperatures. In addition, we report a value for the total deuterium content in the three main stratospheric hydrogen reservoirs HDO, HD, and CH$_3$D of 1.60 ($+0.02/-0.03$) ppbv.   INDEX TERMS: 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 1040 Geochemistry: Isotopic composition/chemistry; 1610 Global Change: Atmosphere (0315, 0325); KEYWORDS: hydrogen isotopic composition, water vapor, stratosphere, tropical troposphere layer

1. Introduction

[2]   It is predicted that the amount of water vapor entering the stratosphere may be altered due to climate-related changes in tropical convection intensity and/or tropical tropopause temperatures [e.g., *Kirk-Davidoff et al.*, 1999]. Changes in stratospheric water vapor may in turn have an impact on tropospheric warming and stratospheric cooling [*Forster and Shine*, 2002; *Oinas et al.*, 2001] and on the concentration of stratospheric HO$_x$ radicals which partici-

pate in catalytic cycles of ozone destruction. The coupling of stratospheric cooling and increased levels of H$_2$O is also predicted to increase the abundance and duration of polar stratospheric clouds [*Tabazadeh et al.*, 2000] and consequently to increase chlorine activation, denitrification, and subsequent O$_3$ loss. An analysis of measurements of water vapor mixing ratios in the stratosphere by satellite and balloon instruments led *Rosenlof et al.* [2001] to suggest that stratospheric water may have increased by approximately 2 ppmv over the last 45 years (or roughly 1%/year).

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Since increases in atmospheric CH_4 are not large enough to account for the reported trend, Rosenlof et al. suggested that changes in the details of the mechanisms controlling the humidity of air entering the stratosphere could be responsible for at least some of the reported change.

[3] Two mechanisms of mass transport in the tropics contribute to the dehydration of air before it enters the stratosphere: rapid vertical motion (of the order of m s^{-1}) in convective systems [e.g., *Danielsen*, 1982] and large-scale slow diabatic ascent (of the order of 10^{-3} m s^{-1}) [e.g., *Brewer*, 1949]. In rapid vertical ascent, energetic convection originating near the surface ascends adiabatically into the tropical tropopause layer (TTL) between ∼14 and 19 km [e.g., *Sherwood and Dessler*, 2000], becoming colder than the surrounding environment and drying the air. Large-scale slow diabatic ascent dehydrates air through freeze-drying at cold TTL temperatures [e.g., *Holton and Gettelman*, 2001]. In general, model studies have focused on the ability of one or the other mechanism to explain observations of water vapor mixing ratios in the TTL [e.g., *Holton and Gettelman*, 2001; *Sherwood and Dessler*, 2000]. However, evidence exists that dehydration may occur with contributions from both mechanisms [e.g., *Dessler*, 2002; *Gettelman et al.*, 2002]. An understanding of the relative contributions of these two processes is necessary in order to investigate the reported change in water vapor [*Rosenlof et al.*, 2001] and to predict how possible changes in convection intensity and detrainment altitude, cloud microphysics, and TTL temperatures may alter the humidity of air entering the stratosphere in the future.

[4] The hydrogen isotopic composition of water vapor in the tropical tropopause layer and stratosphere provides an additional observational constraint, beyond water vapor mixing ratios alone, for determining the relative importance of these two mechanisms of mass transport in dehydrating air. Hydrogen isotopic compositions are generally reported in delta notation, δD, as defined in equation (1).

$$\delta D = \left(\frac{R_{sample}}{R_{std}} - 1 \right) \times 1000 \qquad (1)$$

For water, R_{sample} represents the D/H ratio in a water sample and R_{std} is the D/H ratio for the international reference material Vienna standard mean ocean water (VSMOW); thus the delta value for water, denoted here as δD-H_2O, represents the deviation of the D/H ratio of a water sample from that of the VSMOW standard, expressed in "per mil" (‰). Values for δD-H_2O_0 (where the subscript 0 refers to the tropopause) inferred from remote sensing observations of δD-H_2O in the lower and middle stratosphere are depleted relative to surface observations. For example, *Moyer et al.* [1996] estimated a value for δD-H_2O_0 of -670 ± 80‰ (1σ), while *Johnson et al.* [2001b] inferred a value of -679 ± 20‰ (1σ). One-dimensional (1-D) models simulating the vertical distribution of water and its isotopes predict that water vapor dehydrated only by large-scale slow diabatic ascent of air should have even larger depletions in deuterium, with values for δD-H_2O_0 of -900‰ [*Dessler and Sherwood*, 2003; *Johnson et al.*, 2001a; *Keith*, 2000; *Moyer et al.*, 1996]. The extreme depletion in these models is caused by partitioning between the vapor and ice phases according to the large equilibrium fractionation factor of 1.3 to 1.4 (as extrapolated

from *Merlivat and Nief* [1967]) in a Rayleigh fractionation process as air slowly ascends through the TTL, coupled with the assumption that the ice particles settle out of the air mass completely. In contrast, simulations of dehydration including rapid vertical ascent of air by convection in which ice particles do not completely separate from the air mass have resulted in significantly heavier values for δD-H_2O_0, ranging from -650 to -680‰ depending on model parameters [*Dessler and Sherwood*, 2003; *Johnson et al.*, 2001a; *Moyer et al.*, 1996]. Two different fractionation effects in convective dehydration may be responsible. First, the lofting of ice into the TTL during convection may provide a source of water vapor with a heavier isotopic composition characteristic of lower altitudes since this ice can sublimate in the relatively dry TTL [*Dessler and Sherwood*, 2003; *Keith*, 2000; *Moyer et al.*, 1996]. Unfortunately, the microphysical details controlling the isotopic composition of the ice during formation, lofting, and sublimation into dry air in convective systems remain largely unquantified, both theoretically and experimentally [*Dessler and Sherwood*, 2003]. Second, the mixing of extremely dry air from convection detraining into the TTL may reduce the water vapor mixing ratio in the mixed air while changing the isotopic composition of the water vapor very little [*Dessler and Sherwood*, 2003; *Johnson et al.*, 2001a]. Thus mixing of dry and wet air yields water vapor that is less depleted in deuterium relative to air with the same mixing ratio of water that fractionated in an isolated air mass at thermodynamic equilibrium. This reduction in the apparent fractionation factor due to mixing is well known in many isotopic systems [e.g., *Criss*, 1999], including the fractionation of the isotopologues of water (i.e., any of the isotopic analogs of H_2O, including $H_2^{16}O$, $HD^{16}O$, $H_2^{18}O$, etc.) in the atmosphere [see *Dessler and Sherwood*, 2003, and references therein]. From the modeling studies performed to date, it appears that a value for the annual mean hydrogen isotopic composition of water vapor entering the stratosphere (i.e., δD-H_2O_0) provides important mechanistic information about the dehydration processes of air entering the stratosphere.

[5] Three previous studies have reported values for δD-H_2O_0 using relatively low precision remote sensing measurements of the isotopic composition of water vapor in the upper troposphere and stratosphere (±40 to ±100‰ depending on pressure and technique). *Moyer et al.* [1996] and *Johnson et al.* [2001b] used observations of lower and middle stratospheric δD-H_2O to infer δD-H_2O_0 at the tropopause. However, while an annual mean water vapor mixing ratio of approximately 4 ppmv enters the stratosphere through the tropical tropopause [*Kley et al.*, 2000; *Hurst et al.*, 1999], a significant amount of water vapor (up to 4 ppmv) is produced in situ by CH_4 and H_2 oxidation [e.g., *Herman et al.*, 2003; *Hurst et al.*, 1999]. Oxidation of CH_4 and H_2 alters the isotopic composition of stratospheric H_2O from its value at the tropopause. Thus, to obtain δD-H_2O_0 from stratospheric measurements of δD-H_2O requires a correction for water vapor produced by CH_4 and H_2 oxidation. For the Atmospheric Trace Molecules Spectroscopy (ATMOS) measurements taken aboard the space shuttle from 1985 to 1994, the contribution of CH_4 oxidation was accounted for using simultaneous measurements of CH_3D and CH_4 [*Moyer et al.*, 1996], resulting in an inferred value for δD-H_2O_0 of -670 ± 80‰. For the Far Infrared Spectroscopy

(FIRS-2) measurements taken on seven balloon flights from 1989 to 1997, estimates of the contribution of CH_3D and CH_4 were calculated using a photochemical box model [*Johnson et al.*, 2001b] to infer a value for $\delta D\text{-}H_2O_0$ of -679 ± 20‰. Both studies assumed that $\delta D\text{-}H_2$ remained constant in the stratosphere, as suggested by *Irion et al.* [1996] based on analysis of ATMOS measurements of HDO and CH_3D. Finally, *Kuang et al.* [2003] reprocessed TTL measurements of HDO and H_2O taken by the ATMOS mission between $5°$ and $20°N$ in November 1994 using recently measured spectral lines to determine a value for $\delta D\text{-}H_2O$ throughout the TTL of -648 ± 40‰ (note that this value may not represent an annual mean, as the Johnson et al. and Moyer et al. values do).

[6] Recent isotope ratio mass spectrometric measurements on a suite of stratospheric whole air samples from the ER-2 aircraft of the hydrogen isotopic compositions of both CH_4 and H_2 provide high-precision values for the mixing ratios of CH_3D and HD in the stratosphere [*McCarthy et al.*, 2003; *Rahn et al.*, 2003; *Rice et al.*, 2003]. These measurements of $\delta D\text{-}H_2$ and $\delta D\text{-}CH_4$ can be used to infer $\delta D\text{-}H_2O_0$ more accurately and, in some cases, more precisely than previous studies based solely on remote observations. In this analysis, the contribution of deuterium from CH_4 and H_2 oxidation to stratospheric $\delta D\text{-}H_2O$ is derived using ER-2 measurements. When combined with the FIRS-2 observations of $\delta D\text{-}H_2O$, we determine the total deuterium content of the three hydrogen reservoirs HDO, HD, and CH_3D. Knowing the total deuterium content, we then infer a value for $\delta D\text{-}H_2O_0$, relevant for the mid to late 1990s, and compare it with the remote sensing estimates. Finally, the potential for using $\delta D\text{-}H_2O_0$ as a means of detecting and monitoring possible changes in the mechanisms for dehydration of air in the TTL is discussed.

2. Measurements

2.1. ER-2 Aircraft Measurements

[7] Whole air samples were collected for both trace gas mixing ratio and isotopic analyses on the NASA ER-2 aircraft using the National Center for Atmospheric Research Whole Air Sampler (NCAR WAS) instrument during three NASA campaigns: the last deployment of the Stratospheric Tracers of Atmospheric Transport (STRAT) mission in December 1996 [e.g., *Andrews et al.*, 2001a]; the Photochemistry of Ozone Loss in the Arctic Region in Summer (POLARIS) mission from April to September 1997 [*Newman et al.*, 1999]; and the Stratospheric Aerosol and Gas Experiment (SAGE) III Ozone Loss and Validation Experiment (SOLVE) mission from January to March 2000 [*Newman et al.*, 2002]. Although the maximum altitude of the ER-2 aircraft is less than 22 km when fully instrumented, in situ CO_2 and SF_6 measurements indicate that air that had descended from much higher altitudes was frequently sampled [e.g., *Andrews et al.*, 2001a]. These samples therefore provide information on isotope fractionation occurring above the ER-2 ceiling.

[8] The WAS instrument is described in detail by *Flocke et al.* [1999]. After sample collection, canisters were shipped to NCAR for measurement of trace gas mixing ratios by gas chromatography (GC). Methane mixing ratios were measured using a Hewlett Packard model 5890 gas chromatograph (Agilent, formerly Hewlett-Packard, San Jose, California) fitted with a flame ionization detector (GC-FID). Calibration is based on the National Institute Standards and Technology (NIST) scale from 913 ± 10 ppbv and 1190 ± 10 ppbv NIST standards. Precision of measurement is better than ± 10 ppbv (1σ). Accuracy is better than ± 20 ppbv (1σ). Measurements of N_2O mixing ratios on the SOLVE whole air samples were made on an HP5890 II + series GC fitted with an electron capture detector (ECD) and measured relative to a 314 ppbv N_2O secondary standard of whole air calibrated against a 300 ppbv National Institute Standards and Technology (NIST) Standard Reference Material (SRM) (2608, ± 1%). The average uncertainty (2σ) for the N_2O mixing ratio data is less than 0.7 ± 0.1%.

[9] Measurements of $\delta D\text{-}CH_4$ were made at the University of California at Irvine. Small aliquots (63 mL) of whole air from the archived flasks were measured on a gas-chromatograph continuous-flow isotope ratio mass spectrometer as described by *Rice et al.* [2001]. The precision of these measurements from a pooled variance estimate is ± 1.3‰ (1σ). Measurements of $\delta D\text{-}H_2$ were made at the California Institute of Technology. Four hundred milliliter aliquots of whole air from the WAS canisters and/or the archived flasks were cryogenically separated, leaving only H_2, He, and Ne in the gas phase. The $\delta D\text{-}H_2$ was then measured using a gas-chromatograph isotope ratio mass spectrometer as described by *Rahn et al.* [2002]. Estimated precision for $\delta D\text{-}H_2$ measurements is ± 7‰. Suspected contamination due to the in-growth of H_2 within sample canisters, a known problem with hydrogen sampling [*Gerst and Quay*, 2000], was detected in two samples [see *Rahn et al.*, 2003], which were removed from this analysis. Mass spectrometric analyses of $\delta^{15}N\text{-}N_2$ were performed at Princeton University for a subset of the whole air samples. Because gravitational fractionation is expected to be negligible in the stratosphere, $\delta^{15}N\text{-}N_2$ should be constant, and any measured changes in the whole air samples should be due solely to air sampling and handling. An upper limit to isotope fractionation due to air sampling and handling for $\delta D\text{-}CH_4$ is <0.1‰ and for $\delta D\text{-}H_2$ is <1 ‰ (M. Bender, personal communication, 2002), both of which are less than the expected measurement precision.

[10] Measurements of $\delta D\text{-}CH_4$ and $\delta D\text{-}H_2$ from *Rice et al.* [2003] and *Rahn et al.* [2003] are plotted against methane mixing ratio in Figure 1. Large kinetic isotope effects in reactions with Cl and OH preferentially oxidize the lighter isotopologues, which enriches the remaining methane and hydrogen relative to their tropospheric values [e.g., *McCarthy et al.*, 2003; *Rahn et al.*, 2003; *Rice et al.*, 2003]. Stratospheric H_2 is also enriched by a large isotopic fractionation factor in the oxidation pathway from CH_4 to H_2 as well as the enrichment of its source CH_4 in older stratospheric air [*Rahn et al.*, 2003]. Values for $\delta D\text{-}CH_4$ range from -90‰ at the tropical tropopause to $+26$‰ in polar air that has descended from higher altitudes. Values for $\delta D\text{-}H_2$ range from 130‰ at the tropical tropopause to 440‰ in polar air, a surprisingly large enrichment of over 300‰. In fact, the ER-2 $\delta D\text{-}H_2$ measurements reveal that stratospheric H_2 is by far the most enriched hydrogen-containing compound found in natural materials on Earth apart from some compounds found in unusual meteorites [see *Rahn et al.*, 2003].

[11] Figure 2 shows the mixing ratios of CH_3D and HD, derived from the measured δD values, plotted as a function of
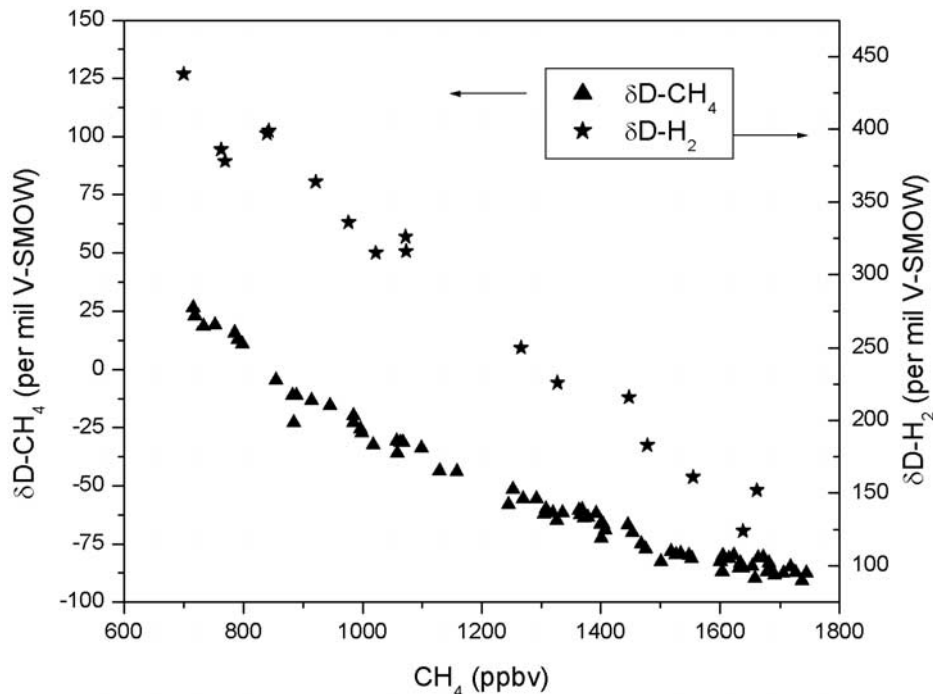
Figure 1. Measurements of δD-H_2 (stars) and δD-CH_4 (triangles) in ‰ on the VSMOW scale on whole air samples collected from the ER-2 aircraft as a function of CH_4 mixing ratio in ppbv from *Rahn et al.* [2003] and *Rice et al.* [2003].

methane mixing ratio. The mixing ratio of CH_3D decreases by a factor of 2 over the range studied, while HD increases by 25%. For comparison, ATMOS remote sensing observations of CH_3D showed a similar trend in mixing ratio through the stratosphere [*Irion et al.*, 1996], although the precision is much lower. For HD, we note that *Irion et al.* [1996] combined the ATMOS observations of CH_3D with HDO to predict that HD (and thus δD-H_2) remains approximately constant, which the ER-2 measurements show is not correct. The apparent discrepancy is due to the lower precision of the ATMOS measurements, which give a possible change in δD-H_2 of ± 6‰ (1σ) for every 1% of CH_3D oxidized. The ER-2 observations show that the actual change in δD-H_2 is near the upper boundary of the Irion et al. estimate, with an increase of +5‰ per 1% of CH_3D oxidized. The important point here is that the previous studies that inferred δD-H_2O_0 [*Johnson et al.*, 2001b; *Moyer et al.*, 1996] from observations of δD-H_2O in the stratosphere assumed HD remained constant based on the *Irion et al.* [1996] results. Properly accounting for the deuterium reservoirs in H_2 and CH_4 with the ER-2 isotope observations should yield a more accurate inference of the value for δD-H_2O_0.

2.2. FIRS-2 Balloon Measurements

[12] A number of measurements of δD-H_2O in the stratosphere are available from various remote sensing instruments and different platforms [e.g., *Johnson et al.*, 2001b; *Stowasser et al.*, 1999; *Moyer et al.*, 1996; *Dinelli et al.*, 1991, 1997; *Rinsland et al.*, 1984, 1991] as well as a single study that obtained stratospheric air samples by cryogenic collection followed by mass spectrometric analysis of the collected water vapor [*Pollock et al.*, 1980]. For this analysis, any of the remote sensing water isotope measurements that were made in conjunction with simulta-

neous measurements of long-lived tracers such as N_2O, CH_4, or SF_6 can be used (note that the single sampling study was affected by contamination problems [*Ehhalt et al.*, 2002]). Because of its relatively good vertical resolution ($\sim$1 km) and the availability of simultaneous measurements of N_2O, we use the Smithsonian Astrophysical Observatory far infrared spectrometer (FIRS-2) observations from a balloon-based platform as published by *Johnson et al.* [2001b]. FIRS-2 is a remote-sensing Fourier transform spectrometer that measures the thermal emission from the atmosphere. The measurements were made during six balloon flights near 33°N between 1989 and 1994 and a single balloon flight at 68°N in 1997. In general, uncertainties in line strengths result in errors in the infrared retrievals of mixing ratios of H_2O and HDO [*Toth*, 1999, 1998]. For the Johnson et al. data set, the resulting uncertainties are believed to be less than 3% [*Johnson et al.*, 2001b]. In addition, systematic errors increase at low altitudes due to pressure broadening effects. Moreover, low-altitude measurements may be subject to biases due to the seasonal cycle in water vapor mixing ratios (and, presumably, a seasonal cycle in δD-H_2O) entering the stratosphere [e.g., *Weinstock et al.*, 2001; *Boering et al.*, 1995; *Mote et al.*, 1995]. The impact of these uncertainties on our analysis will be addressed in section 4. To relate the ER-2 measurements to the FIRS-2 measurements, δD-H_2O observations from the FIRS-2 instrument have been binned and averaged into 20 ppbv N_2O mixing ratio bins as described by *Johnson et al.* [2001b].

3. Analysis

[13] As air ages in the stratosphere, both CH_4 and H_2 oxidation alter the isotopic composition of water vapor from
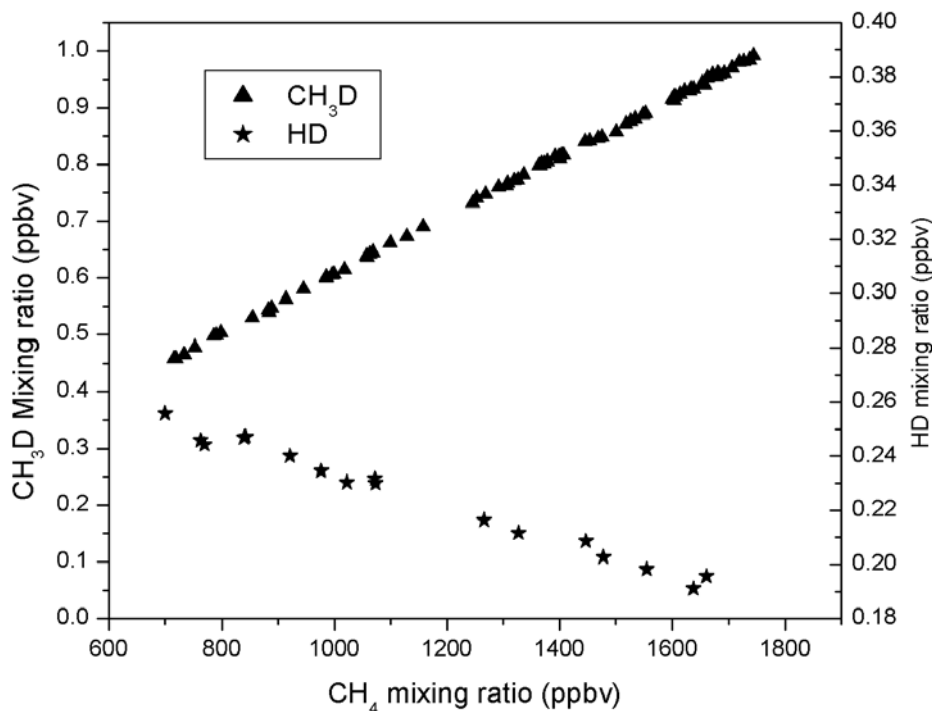
Figure 2. Measurements from Figure 1 converted to mixing ratios of HD (stars) and CH_3D (triangles) mixing ratios as a function of measured CH_4 mixing ratios.

its value at the tropopause. Using the high-precision ER-2 measurements for δD-CH_4 and CH_4 mixing ratios [*Rice et al.*, 2003], δD-H_2 [*Rahn et al.*, 2003], and the correlations among CH_4, H_2, and H_2O mixing ratios [*Herman et al.*, 2003; *Hurst et al.*, 1999], an empirical expression can be derived that accounts for changes in stratospheric δD-H_2O due to the photochemical aging of air based on the fact that the total deuterium content in these three reservoir species remains constant. When combined with extratropical strato-spheric FIRS-2 δD-H_2O observations, this expression can be used to infer a value for the annual mean hydrogen isotopic composition of water vapor entering the strato-sphere (δD-H_2O_0) based solely on observations. A photo-chemical model including all isotope effects for CH_4 and H_2 oxidation by OH, Cl, and $O(^1D)$ and their temperature dependence throughout the stratosphere is therefore not required. Moreover, this study is the first to properly account for the increase in HD in the stratosphere when inferring δD-H_2O_0. Assumptions involved in deriving this empirical expression are noted as they are made; uncertain-ties in the derived value for δD-H_2O_0 are addressed in section 4, and implications will be discussed in section 5.

[14] In the following treatment, we derive an empirical expression for the total deuterium content, D_{total}, of the three main stratospheric reservoirs for deuterium, H_2O, CH_4, and H_2, and then derive an expression for δD-H_2O, constrained by D_{total}, which can be empirically extrapolated back to the tropopause. This approach is taken, rather than a derivation of isotope fractionation factors for H_2O produced from either CH_4 or H_2 oxidation since there is no way a priori to separate the contributions of the different CH_4 and H_2 fractionation factors to the observed overall change in δD-H_2O. The derivation is as follows. First, we note that the

hydrogen isotopic composition of H_2O was given earlier in equation (1) and that the value for R_{std} used is that of VSMOW (multiplied by 2 to account for the two hydrogen atoms, or 0.00031152 [*Hagemann et al.*, 1970]). Second, an empirical expression for the budget of water vapor for extravortex air in the stratosphere measured by *Hurst et al.* [1999] using in situ measurements of CH_4, H_2, and H_2O mixing ratios aboard the ER-2 aircraft during the STRAT and POLARIS campaigns is given by equation (2):

$$H_2O_{eqv} = 1.973 \times CH_4 + H_2O = 7.4 \pm 0.5 \text{ ppmv} \quad (2)$$

where H_2O_{eqv} refers to "equivalent water" [*Herman et al.*, 2003] and italicized chemical formulas are variables representing the value for the mixing ratio of that chemical species. This quantity in equation (2) was previously referred to as "total hydrogen," which was a misnomer since it ignores the molecular hydrogen reservoir of ~0.5 ppmv [e.g., *Hurst et al.*, 1999]; hence we will use the more recent term "equivalent water" here. Note that the deviation of 1.973 from a value of 2 in the expression for H_2O_{eqv} represents the production of H_2 from the oxidation of CH_4. Equivalent water is conserved in the stratosphere except where water is lost, e.g., due to ice formation and gravitational settling in the winter vortices or due to photolysis in the upper stratosphere. These irreversible water sinks are rare at ER-2 altitudes, and the few documented observations of Arctic dehydration were removed from determination of values for H_2O_{eqv} from the STRAT, POLARIS, and SOLVE campaigns [*Herman et al.*, 2003; *Hurst et al.*, 1999]. For comparison, *Herman et al.* [2003] report a value for H_2O_{eqv} of 7.35 ± 0.10 ppmv for the SOLVE campaign. Analyses of remote sensing

observations from balloon platforms have yielded values for H_2O_{eqv} of 7.2 ± 0.6 ppmv [Zoger et al., 1999] and 7.25 ± 0.2 ppmv [Stowasser et al., 1999]. All of these studies agree to within their 1σ uncertainties. The impact of these and other uncertainties in H_2O_{eqv} on our analysis will be addressed in section 4.

[15] A recent study redefined the term "total hydrogen" to include H_2, as shown in equation (3) [Herman et al., 2003]:

$$H_{total} = H_2O + 2 \times CH_4 + H_2 = 7.96 \pm 0.11 \text{ ppmv} \quad (3)$$

Since "total hydrogen" in the stratosphere is conserved, total deuterium should also be conserved. Essentially all deuterium (denoted here as D_{total}) in the lower and middle stratosphere resides in the three reservoir species HDO, CH_3D, and HD. Multiply deuterated species (e.g., CH_2D_2) are assumed to be negligible. "Total deuterium" can therefore be expressed as the sum of all significant deuterated species in the stratosphere (equation (4)).

$$D_{total} = HDO + CH_3D + HD \quad (4)$$

Expressions for CH_3D and HD as a function of CH_4 mixing ratio can be derived from fits to the ER-2 observations shown in Figure 2. Thus since D_{total} is conserved, all that is needed, in principle, to constrain D_{total} throughout the stratosphere is a single value for HDO at a known mixing ratio of CH_4.

[16] The equations for equivalent water (equation (2)) and total deuterium (equation (4)) can be rearranged to yield expressions for H_2O and HDO, respectively. Substituting these expressions for H_2O and HDO into equation (1) yields equation (5):

$$\delta D_{H_2O} = \left(\frac{\frac{D_{total} - CH_3D - HD}{H_2O_{eqv} - 1.973 \times CH_4} - 1}{R_{std}} \right) \times 1000 \quad (5)$$

As noted above, the variables CH_3D and HD in equation (5) can be determined as functions of CH_4 to reduce equation (5) to a dependence on a single unknown parameter, D_{total}. From a fit to the ER-2 measurements in Figure 2, CH_3D as a function of CH_4 is given by equation (6).

$$CH_3D = 5.16 \times 10^{-4} \times CH_4 + 0.0908 \quad (6)$$

The CH_3D:CH_4 relationship is effectively linear over the range sampled by the ER-2 WAS measurements, with an R^2 value of 0.9997. To obtain HD, a linear fit to the ER-2 measurements as a function of CH_4 in Figure 2 yields equation (7) (with $R^2 = 0.986$);

$$HD = -6.32 \times 10^{-5} \times CH_4 + 0.297 \quad (7)$$

Substituting the expressions for HD and for CH_3D into equation (5) yields equation (8), which expresses δD-H_2O as a function of CH_4 and total deuterium, D_{total}:

$$\delta D_{H_2O} = \left(\frac{\frac{D_{total} - [0.000516 CH_4 + 0.0908] - [-0.0000632 CH_4 + 0.297]}{H_2O_{eqv} - 1.973 CH_4} - 1}{R_{std}} \right)$$
$$\times 1000 \quad (8)$$

The only unknown parameter in this expression is D_{total} as defined in equation (4).

[17] As noted earlier, to obtain a value for the conserved quantity D_{total}, at least one value for δD-H_2O at a known CH_4 mixing ratio is needed. For the FIRS-2 δD-H_2O observations, simultaneous measurements of CH_4 mixing ratios are not available for most of the balloon flights, but simultaneous measurements of N_2O were always made. Thus, using the known relationship between the two long-lived tracers CH_4 and N_2O, the FIRS-2 δD-H_2O data can be mapped onto the ER-2 measurements in CH_4 tracer space. Equation (9) is an empirical fit to the CH_4:N_2O relationship measured on the SOLVE whole air samples collected from the ER-2 aircraft (see Figure 3).

$$CH_4 = 3.95 \times N_2O + 498 (\text{ppbv}) \quad (9)$$

This linear CH_4:N_2O relationship is characteristic of vortex air, which is a mixture of midlatitude air from the middle and lower stratosphere [Michelsen et al., 1998]. A curvilinear midlatitude CH_4:N_2O relationship from the Michelsen et al. ATMOS measurements can also be used (see dashed line in Figure 3; the dotted line is the tropical CH_4:N_2O relationship, which is not relevant for this study since all measurements are in air masses of extratropical character). Uncertainties in δD-H_2O_0 as a result of using either the ER-2 vortex or the ATMOS midlatitude CH_4:N_2O relationship to map the FIRS-2 δD-H_2O observations onto the ER-2 CH_4 measurements will be discussed in section 4. We note here that the FIRS-2 measurements were taken primarily at midlatitudes from a balloon gondola, while the ER-2 observations range from the tropics to 89°N from 8 to 21 km. The two measurement sets do overlap to some degree, however, since the latest FIRS-2 balloon flight coincided with the POLARIS mission in 1997, sampling the same air masses in the lower stratosphere and exhibiting similar tracer/tracer relationships throughout the respective flights. Other studies have shown that balloon and ER-2 observations exhibit very similar long lived tracer/tracer correlations despite differences in the altitude of the measurements [e.g., Daube et al., 2002; Andrews et al., 2001a, 2001b; Rex et al., 1999; Herman et al., 1998].

[18] To estimate the annual mean isotopic composition of water vapor at the tropical tropopause, we first use individual FIRS-2 δD-H_2O observations in equation (8) to estimate a value for D_{total} in the stratosphere. With a value for D_{total}, we then use equation (8) to calculate δD-H_2O at a CH_4 mixing ratio of 1710 ppbv, the average CH_4 mixing ratio at the tropical tropopause for these data sets, a value which will be discussed further below. The calculated value of δD-H_2O for $CH_4 = 1710$ ppbv is thus an estimate for δD-H_2O_0, the annual mean isotopic composition of water vapor entering the stratosphere for the time period covered by the observations. Figure 4 shows the FIRS-2 δD-H_2O observations as solid triangles along with their 1σ error bars. The solid lines in Figure 4 emanating from each of the FIRS-2 binned data points are the values for δD-H_2O as a function of CH_4 mixing ratio calculated from equation (8) using a single FIRS-2 δD-H_2O observation to first constrain D_{total}. The values for D_{total} from the individual FIRS-2 data points range from 1.67 to 1.58 ppbv. These in turn yield estimates for δD-H_2O_0 ranging from -594 to -671‰ at a
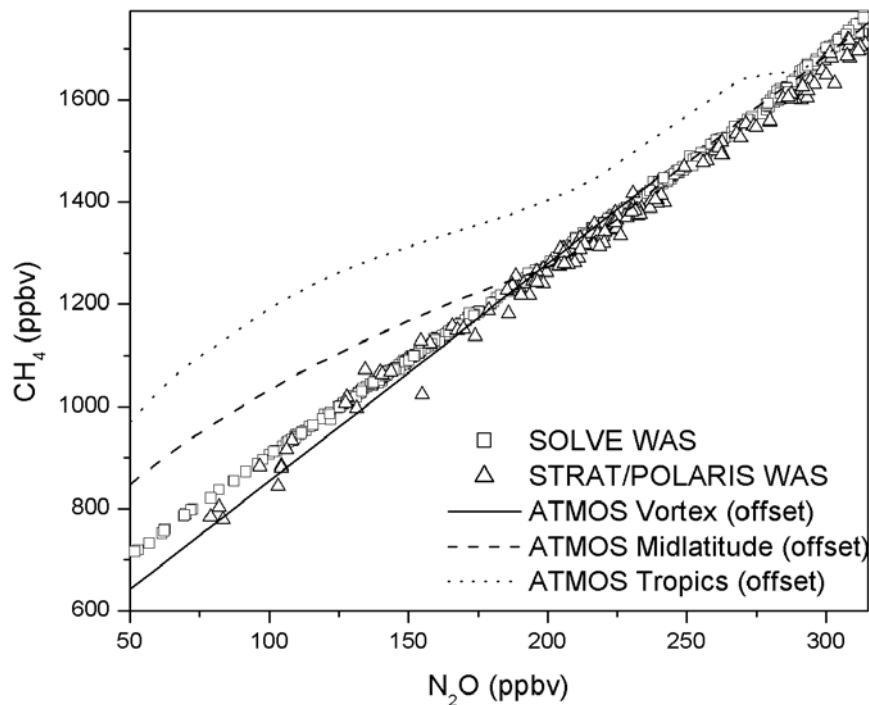
Figure 3. CH_4 versus N_2O mixing ratios from ER-2 whole air samples from STRAT, POLARIS, and SOLVE (symbols) and from ATMOS satellite observations from *Michelsen et al.* [1998] (lines); ATMOS CH_4 mixing ratios are offset by +40 ppbv to account for the CH_4 growth rate between the time of the ATMOS and ER-2 observations. The difference between the midlatitude (dashed line) and vortex CH_4:N_2O relationships was fit to a third-order polynomial ($CH_4 = 9.53 \times 10^{-5}N_2O^3 - 4.48 \times 10^{-02}N_2O^2 + 5.26N_2O - 44.2$) and added to equation (9) for the uncertainty analysis (see text).

tropopause boundary of 1710 ppbv CH_4. The mean value for δD-H_2O_0 using this series of measurements is $-651‰$ with a standard deviation of 20‰. The heaviest value for δD-H_2O_0 originates from the lowest CH_4 mixing ratio/ highest altitude FIRS-2 point and is more than 40‰ heavier than any other, a point discussed further below. Thus, although in principle only one observation of δD-H_2O is needed to constrain D_{total} in equation (8) before using it to extrapolate δD-H_2O to the tropopause, uncertainties in the remote observations, and perhaps in correlating the remote and ER-2 observations, make it preferable to obtain a value for D_{total} using the entire FIRS-2 δD-H_2O data set.

[19] A more robust value for D_{total} using the entire set of δD-H_2O observations, rather than a single observation, and their uncertainties can be estimated by fitting the relationships in equation (8) using a nonlinear least squares fitting function based on the Levenberg-Marquart algorithm. This nonlinear fit to equation (8) weights the FIRS-2 δD-H_2O observations by $1/\sigma^2$ where σ is given by the error bars in Figure 5. Using the entire set of FIRS-2 observations improves the uncertainty in the estimates for D_{total} and δD-H_2O_0 relative to using a single point. Moreover, the $1/\sigma^2$ weighting means that the least uncertain (highest altitude) measurements receive the most weight; coincidentally, these are also the data points for which the seasonal cycle in water vapor mixing ratios (or for δD-H_2O) should be damped out (which is discussed further below). The best fit value for D_{total} using this method is 1.60 (+0.02/−0.03) ppbv. For a CH_4 mixing ratio of 1710 ppbv at the tropical

tropopause, the value of δD-H_2O_0 is -653 ‰ (see Figure 4). The uncertainty from the fitting procedure alone is $\pm$ 2‰, much improved over the 20‰ standard deviation noted above using individual FIRS-2 measurements. When all known uncertainties are summed in quadrature, the overall 1σ uncertainty is +24/−25‰. This estimate includes the uncertainty in the fit for D_{total} as well as uncertainties in other derived quantities in equation (8) and a possible 3% uncertainty in the infrared retrievals for H_2O and HDO. Each of these uncertainties will be discussed in more detail in section 4. This best fit value for δD-H_2O_0 of -653 (+24/−25)‰ is 20−30‰ heavier than those inferred by *Johnson et al.* [2001b] and *Moyer et al.* [1996] and 5‰ lighter than the value for δD-H_2O measured by *Kuang et al.* [2003] in November 1994 in the TTL. Although all of these values overlap within their stated uncertainties, we show next that there is a systematic difference between the mean values derived for δD-H_2O_0 by Moyer et al. and Johnson et al. and the mean value derived here for which changes in δD-H_2 have been taken into account.

[20] In order to quantify the impact of δD-H_2 on the stratospheric δD-H_2O calculations, equation (8) was modified such that δD-H_2 remained constant, as was assumed in the *Moyer et al.* [1996] and *Johnson et al.* [2001b] studies. The dotted lines in Figure 4 show the calculated values for δD-H_2O when δD-H_2 is held constant and D_{total} is constrained by individual, binned FIRS-2 data points. Relative to the solid lines in Figure 4 calculated from equation (8), holding δD-H_2 constant results in values for δD-H_2O_0 that
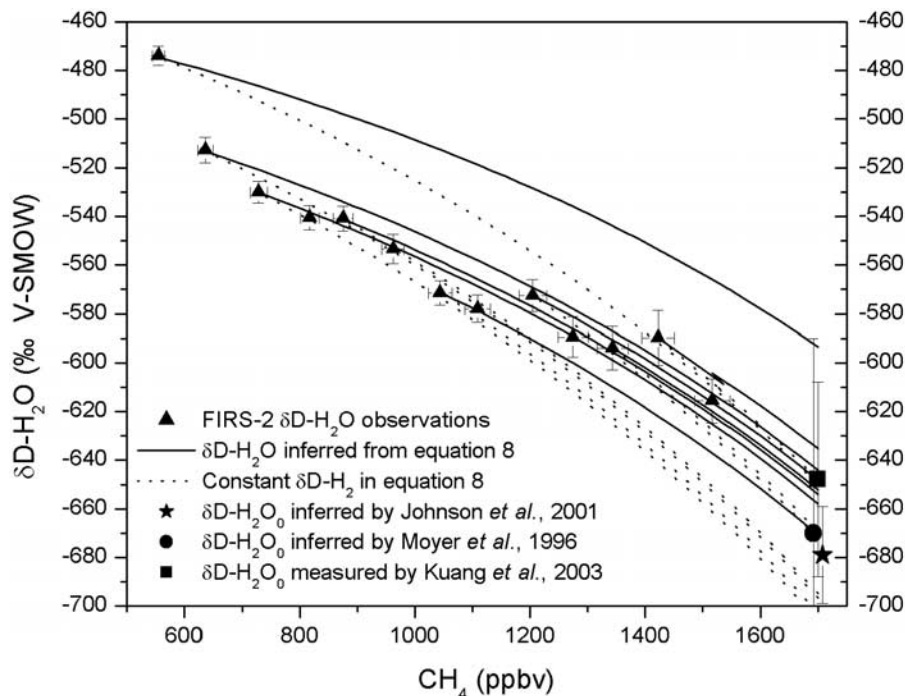
Figure 4. Measurements of δD-H_2O from the FIRS-2 instrument are shown as triangles with 1σ error bars after binning and averaging with respect to N_2O. Solid lines show δD-H_2O values calculated from equation (8) after equation (8) is applied to the individual FIRS-2 observations to obtain individual values for D_{total}. Dotted lines show δD-H_2O calculated from a modified equation (8) that assumes the value of δD-H_2 remains constant in the stratosphere at its tropospheric value. Previous estimates of δD-H_2O_0 and their 1σ error bars are also shown (the square, circle, and star at 1710 ppbv CH_4).

are lighter by as much as 55‰. Moreover, the change in estimated δD-H_2O_0 becomes larger at higher altitudes where the measurement precision is highest. Holding δD-H_2 constant yields an average δD-H_2O_0 value of -689 ± 20‰. This value of δD-H_2O_0 is closer to the value of -679 ± 20‰ reported by *Johnson et al.* [2001b], which is consistent with their assumption that δD-H_2 is constant in the stratosphere.

[21] Reversing the analysis, it is also interesting to set the value of δD-H_2O_0 at the tropopause as the starting point to obtain D_{total}, then use equation (8) to calculate δD-H_2O throughout the rest of the stratosphere. Figure 5 shows the results of using values for δD-H_2O_0 from *Moyer et al.* [1996] (-670‰) and *Johnson et al.* [2001b] (-679‰) to calculate how δD-H_2O evolves in the stratosphere using equation (8). These values for δD-H_2O_0 lead to calculations of δD-H_2O which are too light to match the FIRS-2 observations by 20‰. This difference is also consistent with the magnitude of the error introduced by holding δD-H_2 constant in the stratosphere demonstrated above.

[22] Finally, the solid line in Figure 5 represents values for δD-H_2O calculated from equation (8) using a value for δD-H_2O_0 of -653‰ from the best nonlinear least squares fit of equation (8) to the FIRS-2 measurements described earlier. Using this value for δD-$H2O_0$, the FIRS-2 data are predicted well except for the lowest CH_4 mixing ratio FIRS-2 point, which appears to be an outlier, as it also does in the *Johnson et al.* [2001b] analysis of simultaneous measurements of $\delta^{17}O$ and $\delta^{18}O$ of H_2O. Although we do not exclude this point from the analysis, we do discuss

the sensitivity of our results for δD-H_2O_0 to including or excluding this potential outlier, along with other uncertainties, below.

4. Assessing Uncertainties in Derived δD-H_2O_0

[23] There are seven uncertainties in deriving equation (8) and applying it to the δD-H_2O observations that dominate the overall uncertainty in the estimated value for δD-H_2O_0. These are listed in Table 1. Together, when added in quadrature, these uncertainties yield a 1σ error of ($+24/-25$‰) for δD-$H_2O_0 = -653$‰, and are discussed in detail below. Most of the uncertainties also affect total deuterium so that $D_{total} = 1.60$ ($+0.02/-0.03$) ppbv.

[24] The magnitude and direction of each of these errors are as follows. First, the systematic retrieval errors for the FIRS-2 data of <3% result in a ± 14‰ uncertainty in δD-H_2O (see *Johnson et al.* [2001b] for details). Second, it is possible to map the FIRS-2 δD-H_2O observations to CH_4 using a midlatitude CH_4:N_2O relationship from ATMOS [*Michelsen et al.*, 1998] instead of a high-latitude CH_4:N_2O relationship (equation (9)) from the ER-2 SOLVE, STRAT, and POLARIS campaigns (see Figure 3). Using the ATMOS midlatitude relationship yields a heavier value for δD-H_2O_0 by 10‰ because CH_4 mixing ratios are higher at midlatitudes for a given N_2O mixing ratio. Third, the value chosen for the H_2O_{eqv} mixing ratio defined in equation (2) can affect both D_{total} and δD-H_2O_0. Using the $\pm 1\sigma$ uncertainties in H_2O_{eqv} from *Herman et al.* [2003] results in calculated δD-H_2O_0 values that change by $-12/+8$‰; the difference in
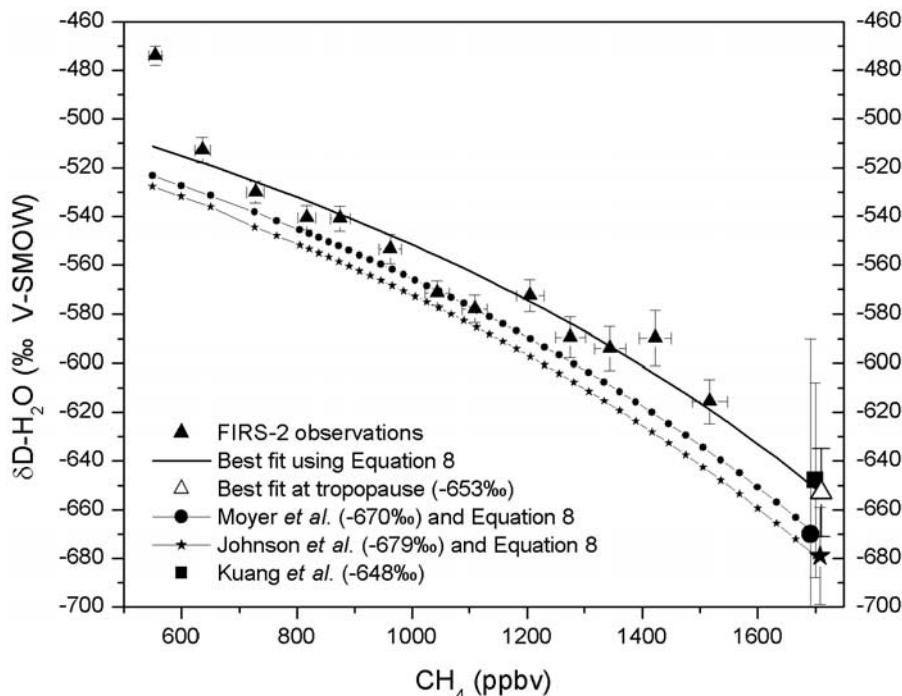
Figure 5. FIRS-2 observations of δD-H_2O are shown as triangles with 1σ error bars after binning and averaging with respect to N_2O. The solid line shows δD-H_2O calculated from equation (8) using the value for D_{total} derived from the best fit of the FIRS-2 observations to equation (8). Using this best fit value for D_{total} and equation (8), δD-H_2O_0 is estimated to be -653 $(+24/-25)$‰ (see text). The solid line with symbols shows the calculated values for δD-H_2O using equation (8) and previous estimates of δD-H_2O_0 to constrain D_{total} in equation (8): circles $= -670$‰ and stars $= -679$‰.

the magnitudes of the positive and negative sensitivities result from coupling between changes in water vapor and D_{total}. We also note that while a trend in H_2O_{eqv} of $+0.04$ to $+0.075$ ppmv/yr has been reported based on remote sensing observations, no trend is observable in ER-2 measurements over the period 1993–2000 [e.g., *Michelsen et al.*, 2000]. If such a trend is real, a small bias in using the FIRS-2 δD-H_2O measurements averaged over 1989–1997 may exist; however, this uncertainty should be small compared with the uncertainty in measuring H_2O and HDO remotely and the uncertainty in the value for H_2O_{eqv}, both of which are already included in our overall uncertainty estimate. Fourth, the uncertainties in the FIRS-2 data set vary with respect to altitude. The FIRS-2 points at the lowest altitudes have the largest uncertainty and so are discounted accordingly in the nonlinear fit used. However, as mentioned earlier, the lowest CH_4 mixing ratio FIRS-2 observation appears to be an outlier as determined by the

95% confidence intervals of a *t*-test as well as on the basis of its $\delta^{17}O$ and $\delta^{18}O$ relationships noted earlier. Excluding this point from the fit yields a lighter value for δD-H_2O_0 by 8‰. It can also be argued that the analysis should not be extrapolated below CH_4 mixing ratios of 700 ppbv, since this is the lowest CH_4 mixing ratio measured for which there are simultaneous observations of δD-CH_4 and δD-H_2 from the ER-2 aircraft. Excluding the two FIRS-2 observations with CH_4 mixing ratios below 700 ppbv yields a lighter value for δD-H_2O_0 by 9‰, an effect not significantly different from excluding only the highest altitude/lowest CH_4 mixing ratio FIRS-2 data point. Fifth, there is uncertainty in the value selected for the mixing ratio of CH_4 entering the stratosphere, defined here as $(CH_4)_0$. Since CH_4 at the surface has increased from the early 1990s (when most FIRS-2 observations were taken) to the late 1990s (ER-2 measurements), there may be a discrepancy in the two measurement sets. In their estimate

Table 1. Uncertainties in Derived Value for δD-H_2O_0

Parameter	Uncertainty in Parameter	Resulting Uncertainty in δD-H_2O_0 (1σ)
FIRS-2 retrieval error	<3%	±14‰
CH_4:N_2O mapping	midlatitude versus vortex	+10‰
H_2O_{eqv}	+0.09/−0.15 ppmv	−12‰/+8‰
FIRS-2 outliers	excluding highest altitude points	−8‰ (−9‰)
CH_4 at tropopause	±20 ppbv	−4‰/+5‰
CH_3D at tropopause	±0.015 ppbv	±12‰
H_2 at tropopause	±10 ppbv	±1‰
HD at tropopause	±0.01 ppbv	±8‰
Overall estimate		+24‰/−25‰

for δD-H_2O_0, *Johnson et al.* [2001b] used a value of 1710 ppbv for $(CH_4)_0$; this value is the same as the average of the CH_4 mixing ratios measured in the WAS tropical tropopause samples from STRAT and POLARIS. Moreover, even though higher CH_4 mixing ratios near the global average surface value of 1735 ppbv for the year 2000 [*Dlugokencky et al.*, 2001] were observed in 1999-2000 during SOLVE in the extratropical lowermost stratosphere, there is no discernable difference in the δD-CH_4:CH_4 relationship for the SOLVE samples versus those from STRAT and POLARIS; thus we do not expect that a temporal change in $(CH_4)_0$ between the FIRS-2 and the ER-2 STRAT, POLARIS, and SOLVE data sets has a significant impact on the analysis here. For completeness, we note that the sensitivity of δD-H_2O_0 calculated from equation (8) to a change of ± 20 ppbv in $(CH_4)_0$ is $-4\permil/+5\permil$.

[25] The other remaining uncertainties are the values for CH_3D, H_2, and HD at the tropopause, which convolve uncertainties in the various fits to CH_4 used in the analysis, the δD isotope measurements themselves, and knowledge of the tropopause value for CH_4. The associated uncertainties are given in Table 1. Other possible uncertainties are likely smaller than seven of the eight of those noted in Table 1. For example, the seasonal cycle in H_2O entering the stratosphere is completely attenuated for $CH_4 < 1250$ ppbv [*Herman et al.*, 2003], which should also be true for a possible seasonal cycle in δD-H_2O at the tropopause. Using only FIRS-2 observations with $CH_4 < 1250$ ppb changes δD-H_2O_0 by less than 2‰. This change is small at least in part because the low-altitude points were weighted less due to their larger error bars. Finally, we also note that the overall uncertainty was estimated as a sum in quadrature of the eight uncertainties given in Table 1. This estimate is likely a conservative one, given that some of the uncertainties noted are coupled but are treated independently.

5. Discussion

[26] The analysis in section 3 yields an estimate for D_{total} of 1.60 (+0.02/−0.03) ppbv in the stratospheric hydrogen reservoirs HDO, CH_3D, and HD. *Irion et al.* [1996] estimated tropopause values for CH_3D and HD of 0.99 ± 0.08 and 0.167 ± 0.05 ppbv, respectively, from ATMOS measurements of CH_3D and HDO while our analysis yields values of 0.975 ± 0.015 and 0.190 ± 0.01 ppbv. The Irion et al. analysis agrees with our results within the respective 1σ error bars even though they concluded that HD remains constant (see section 2.1). Previous estimates of HDO at the tropopause calculated from reported δD-H_2O_0 values and annually averaged H_2O mixing ratios entering the stratosphere range from 0.348 ± 0.027 ppbv [*Johnson et al.*, 2001b] to 0.370 ± 0.117 ppbv [*Moyer et al.*, 1996]. Our analysis indicates a value for HDO at the tropopause of 0.435 (+0.021/−0.030) ppbv, which is significantly larger than that predicted by *Johnson et al.* [2001b]. The difference is largely due to the difference in H_2O at the tropical tropopause in the two studies (3.5 versus 4.0 ppmv). Combining previous estimates for the individual reservoirs yields values for D_{total} of 1.50 ± 0.1 and 1.53 ± 0.15 ppbv for the *Johnson et al.* [2001b] and *Moyer et al.* [1996] HDO estimates, respectively. These estimates are smaller than the value for D_{total} of 1.60 (+0.02/−0.03) ppbv derived here,

but are within the 1σ uncertainties. Again, the difference in estimates for D_{total} is primarily due to difference in tropopause values for H_2O and HDO in each study.

[27] Using our value for the total deuterium content, we then calculated a value for the annual mean isotopic composition of water vapor (δD-H_2O_0) of −653 (+24/−25)‰ in section 3. This value is similar to the value for δD-H_2O of −648 ± 40‰ measured directly in the TTL by *Kuang et al.* [2003], although the agreement may be fortuitous if, for example, there is a significant annual cycle in δD-H_2O in the TTL since their observations were made in November. This analysis yields a heavier value on average for δD-H_2O_0 than the −670 ± 80‰ inferred by *Moyer et al.* [1996] and the −679 ± 20‰ inferred by *Johnson et al.* [2001b], although all values are within the 1σ estimated errors. (We note that the ±20‰ value is the estimated accuracy given by *Johnson et al.* [2001b], including estimated uncertainties in the photochemical model used to extrapolate δD-H_2O back to the tropopause and the infrared retrieval errors.) We showed in section 3 that the dominant factor for the discrepancy in the mean values is the treatment of the molecular hydrogen reservoir of deuterium. Our analysis indicates that not including δD-H_2 enrichment yields a value of δD-H_2O_0 that is ∼35‰ lighter than when H_2 enrichment is taken into account. The systematic error of ignoring δD-H_2 in previous inferences accounts for the lighter average values in δD-H_2O_0. This difference is approximately the magnitude of the difference between our best fit value of −653‰ for δD-H_2O_0 and that from the *Johnson et al.* [2001b] analysis of −679‰. It is likely that the ATMOS inference of −670‰ obtained by *Moyer et al.* [1996] should also be increased by ∼30‰ to account for the hydrogen reservoir.

[28] This more accurate and, in most cases, more precise value of −653 (+24/−25)‰ for δD-H_2O_0 provides an important diagnostic for models of the isotopic fractionation of water vapor in the tropical tropopause layer, just as the earlier values estimated by Moyer et al. and Johnson et al. have provided. On the basis of results from 1-D models published to date, the 20−30‰ increase in the value for δD-H_2O_0 from previous studies would appear to further validate the models in which convective processes dominate the dehydration of wet tropospheric air. However, before such a conclusion can be reached, important details remain to be tested in these and increasingly sophisticated models of isotope fractionation and dehydration in convection versus large-scale vertical ascent and combinations of the two. For example, the assumption that ice particles settle out completely from air undergoing large-scale vertical ascent may not always be correct, and the effects of extensive horizontal mixing of air parcels having undergone Rayleigh fractionation under a wide range of temperature histories has not yet been included in the models of large-scale vertical ascent published to date. Incomplete ice settling and inclusion of extensive mixing of air from multiple distillation processes may lead to heavier predicted values for δD-H_2O in the tropical tropopause layer for slow vertical ascent. In addition, while some studies have suggested that lofting of ice and/or convective overshoot appear to be required to produce a heavy value for δD-H_2O_0 [*Dessler and Sherwood*, 2003; *Johnson et al.*, 2001a; *Keith*, 2000; *Moyer et al.*, 1996], preliminary results using the 3-D GISS general

circulation model in which ice lofting and convective overshoot do not occur yield values in the TTL similar to the range of observations discussed here (G. Schmidt, personal communication, 2003). Thus increasingly sophisticated modeling studies [e.g., *Dessler and Sherwood*, 2003; *Gettelman and Kinnison*, 2003; *Schmidt et al.*, 2003; *Smith et al.*, 2003] may benefit from more accurate and precise values for $\delta D\text{-}H_2O_0$ from observations.

[29] The estimate for $\delta D\text{-}H_2O_0$ derived here for the mid to late 1990s also provides a more accurate benchmark value for comparison with future measurements of $\delta D\text{-}H_2O_0$, which may prove to be a sensitive indicator of climate change. If the mechanisms of dehydration in the tropical troposphere depend strongly, for example, on the microphysics of ice formation in clouds, convection intensity and altitude of detrainment, and/or tropical tropopause temperatures, long-term changes in $\delta D\text{-}H_2O_0$ may result. Colder tropical tropopause temperatures might lead to lighter $\delta D\text{-}H_2O_0$ if large-scale slow diabatic ascent is responsible for a significant fraction of dehydration in air entering the stratosphere, while warmer tropopause temperatures may have the opposite effect. If sea surface temperatures increase, stronger and more frequent convection events might be expected, which may penetrate and detrain at higher altitudes in the TTL. This process might loft more ice into the TTL and/or cause further drying from detrainment of desiccated air, causing $\delta D\text{-}H_2O_0$ to become heavier or to remain at a level similar to what is observed today. Combined with measurements of H_2O_0, long-term monitoring of $\delta D\text{-}H_2O_0$ could be useful for early detection and monitoring of changes in details of the processes that control stratospheric humidity that may be sensitive to climate change. Moreover, in the near future, high-resolution in situ measurements will directly reveal the seasonal, longitudinal, and latitudinal variations in $\delta D\text{-}H_2O$ throughout the tropical tropopause layer [e.g., *Webster and Heymsfield*, 2003]. The analysis and measurements presented here provide a complementary technique for determining a precise and accurate value for the annual mean isotopic composition of water vapor entering the stratosphere.

6. Summary

[30] Precise and accurate measurements of $\delta D\text{-}H_2$ and $\delta D\text{-}CH_4$ from whole air samples collected from the ER-2 aircraft, combined with remote observations of $\delta D\text{-}H_2O$ from the FIRS-2 spectrometer, were used to calculate a value for the total deuterium content in the stratospheric reservoirs HDO, HD, and CH_3D of 1.60 (+0.02/−0.03) ppbv and to account for the effects of H_2 and CH_4 oxidation on the hydrogen isotopic composition of stratospheric H_2O. Applying an empirically derived expression to FIRS-2 remote observations of $\delta D\text{-}H_2O$ yielded an annual mean value for $\delta D\text{-}H_2O_0$ of −653 (+24/−25‰) for the mid to late 1990s. This estimate is ~20‰ heavier and more accurate than earlier inferences based on remote sensing observations alone for approximately the same time period. Properly accounting for the very large enrichment in stratospheric $\delta D\text{-}H_2$ is responsible for the bulk of this difference. Overall, this analysis provides a precise and accurate benchmark value for the annual mean hydrogen isotopic composition of water vapor entering the stratosphere. Future observations can be com-

pared with this value with the potential for monitoring the impacts of climate change on water vapor mixing ratios and isotopic compositions entering the stratosphere.

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