Stratospheric observations of CH₃D and HDO from ATMOS infrared solar spectra: Enrichments of deuterium in methane and implications for HD


Abstract. Stratospheric mixing ratios of CH₃D from 100 mb to 17 mb (=15 to 28 km) and HDO from 100 mb to 10 mb (=15 to 32 km) have been inferred from high resolution solar occultation infrared spectra from the Atmospheric Trace Molecule Spectroscopy (ATMOS) Fourier-transform interferometer. The spectra, taken on board the Space Shuttle during the Spacelab 3 and infrared solar spectra: Enrichments of deuterium in the mid to lower stratosphere, the average lifetime of CH₃D is found to be (1.19±0.02) times that of CH₄, resulting in an increasing D/H ratio in methane as air "ages" and the methane mixing ratio decreases. We find an average of (1.0±0.1) molecules of stratospheric HDO are produced for each CH₃D destroyed (1σ combined precision and systematic error), indicating that the rate of HDO production is approximately equal to the rate of CH₃D destruction. Assuming negligible amounts of deuterium in species other than HDO, CH₃D and HD, this limits the possible change in the stratospheric HD mixing ratio below about 10 mb to be ±0.1 molecules HD created per molecule CH₃D destroyed.

Introduction

In the stratosphere, H₂O is created primarily by oxidation of CH₄ and H₂ by OH, Cl and O(1D). Likewise, oxidation of CH₃D and HD creates HDO, but these deuterated species show a sufficiently different reactivity with surrounding chemical species so that their measurement can provide additional insight into the stratospheric hydrogen budget. In understanding the deuterium budget of the stratosphere and relating it to the hydrogen budget, several questions arise. First, what is the lifetime of CH₃D compared to that of CH₆, or put another way, how does the D/H ratio in methane vary with the CH₄ mixing ratio? Second, is the rate of stratospheric HDO production balanced by that of CH₃D oxidation? If not, could there be a net production or destruction of HD, and possibly a change in the D/H ratio of molecular hydrogen, due to a difference in the rates between CH₃D oxidation to HD and HD oxidation to HDO? (Discussion of the D/H ratio in stratospheric water is in an accompanying paper by Moyer et al. [this issue].) We address these questions using spectroscopic measurements of stratospheric CH₃D and HDO mixing ratios using data from the ATMOS instrument. ATMOS, described in detail by Farmer et al. [1987], is a Fourier-transform infrared interferometer that gathered spectral absorption measurements at 0.01 cm⁻¹ resolution from solar occultations on board four Space Shuttle missions (see Gunson et al. [this issue]). A previous report of HDO and CH₃D results from ATMOS was made by Rinsland et al. [1991] with data from the Spacelab 3 mission; however, their report did not relate changes in the CH₃D mixing ratio to those in HDO. With the combined Spacelab 3 and ATLAS-1, -2, and -3 missions, a much broader latitudinal coverage and many more vertical mixing ratio profiles were obtained, allowing characterization of the CH₃D and HDO budget on a more global basis. An important addition to previous reports is measurement of CH₃D inside the Arctic and Antarctic vortices. Above 28 km, the molecular density of CH₃D is normally too low to gain an adequate spectral absorption signal with the ATMOS instrument. However, the descent of upper stratospheric air to altitudes below 28 km inside the vortices [Abrams et al., this issue a,b] allows measurement of CH₃D in "old" air that would be otherwise impossible to measure. As stratospheric dehydration is not the focus of this letter, we do not report measurements of HDO inside the polar vortices. Analyses are continuing on these vortex HDO measurements, and they will be the focus of an upcoming paper.

In this paper, the delta notation is used to describe isotopic fractionation as the difference in parts per thousand of an isotopically labelled species with respect to a standard, e.g.,

\[ \delta_{sample} (\%o) = \frac{(D/H)_{sample} - (D/H)_{standard}}{(D/H)_{standard}} \times 10^3 \]  

(1)

Standard Mean Ocean Water (SMOW) is used for the standard D/H ratio (see IUPAC [1983]) and we use the recommended value of (155.76±0.05)×10⁻⁶ [Hagemann et al., 1970].

Observations and data analysis

Information about ATMOS on the shuttle missions, and discussion of the mixing ratio retrieval process, can be found in Gunson et al. [this issue]. For the results described here, spectral lines of the ν₂ band of HDO and the ν₁ band of CH₃D were analyzed, and spectral intervals used for these analyses are described in Table 1. HDO is best observed in filters 2 (1100-
oxidation of CH₃D and CH₄ can then be described by:

\[ \text{OH, C1, and O(1D) oxidation, and photolysis is negligible. The effects on the D/H ratio of methane, we begin by assuming that in } \]

than those for CH₄ \cite{DeMore et al., 1994; Wallington and Hurley, 1992}, but any isotope effect between the rate constants of the

in line intensities, are estimated to be 7% for CH₃D, 6% for HDO, and 5% for CH₄ \cite{Abrams et al., this issue, c}. The filter 2 and 9 HDO data. Systematic biases, mostly from errors

for CH₃D and HDO, or 10% for CH₄. This step eliminated about 16% of the filter 3 CH₃D data and about 19% of the

mixing ratios inside the vortex than outside at

similar altitudes (see Abrams et al., this issue a,b). "Vortex edge" mixing ratio profiles of CH₄ and N₂O, as these gases show

2000 cm⁻¹ and 9 (600-2450 cm⁻¹), while CH₃D could only be observed in filter 3 (1350 - 3400 cm⁻¹). However, CH₄ can be analyzed in all of these filters and, with a correlation of CH₃D to CH₄ in filter 3, we are able infer the mixing ratio of CH₃D in filters 2 and 9 from CH₄ mixing ratios. At polar latitudes, determination as to whether a CH₃D measurement was inside or outside the vortex was based on visual inspection of co-located mixing ratio profiles of CH₄ and N₂O, as these gases show markedly smaller mixing ratios inside the vortex than outside at similar altitudes \cite{Abrams et al., this issue, a,b}. "Vortex edge" observations were not used. CH₃D results are presented from tangent pressures of 100 mb to 17 mb, and HDO results are from 100 mb to 10 mb. Before final analyses, data were filtered by rejecting any observations with an estimated random error greater than 30% for CH₃D and HDO, or 10% for CH₄. This step

Note: The temperature dependence for air-broadened half-widths is T⁻⁰.⁷₅

for CH₃D and T⁻⁰.⁶₄ for HDO. Line parameters are discussed in Brown et al. \cite{1995}.

\[ \frac{1}{[\text{CH}_3D]} \frac{d[\text{CH}_3D]}{dt} = -k_{\text{OH}}[\text{OH}] - k_{\text{Cl}}[\text{Cl}] - k_{\text{O(1D)}}[\text{O(1D)}], \]

\[ \frac{1}{[\text{CH}_4]} \frac{d[\text{CH}_4]}{dt} = -k_{\text{OH}}[\text{OH}] - k_{\text{Cl}}[\text{Cl}] - k_{\text{O(1D)}}[\text{O(1D)}]. \]

\[ \frac{1}{[\text{CH}_3D]} \frac{d[\text{CH}_3D]}{dt} = - (\gamma_{\text{OH}} - 1) k_{\text{OH}}[\text{OH}] - (\gamma_{\text{Cl}} - 1) k_{\text{Cl}}[\text{Cl}] - (\gamma_{\text{O(1D)}} - 1) k_{\text{O(1D)}}[\text{O(1D)}]. \]

We emphasize that this is only a rough estimation as none of the experiments measuring the kine-
The mixing ratio of CH₃D and CH₄ are plotted against each other in Figure 1. We assume that χ(CH₄) = (1.71±0.03) x 10⁻⁶ (from a best fit line of ln χ(CH₃D) vs ln χ(CH₄), we observe Kᵥ = (0.84±0.02) (1σ combined precision and systematic error), which is higher than our initial estimate of 0.78. Note the error in Kᵥ is not affected by systematic errors in the measured stratospheric mixing ratios of CH₃D and CH₄ (which instead affect the error in the intercept). The average, the stratospheric lifetime of CH₃D should be equal to the number of times that of CH₄, or about 190 years based on a stratospheric CH₄ lifetime of 160 years (Prather and Spivakovsky, 1990). From the fitted line at a tropospheric CH₄ mixing ratio of (1.71±0.03)x10⁻⁶, we find the mixing ratio of CH₃D entering the stratosphere to be (9.9±0.8)x10⁻¹⁰ (1σ combined precision and systematic error).

The lower panel of Figure 1 shows the enrichment of CH₃D with CH₄ mixing ratio, as well as the average enrichment calculated using the fitted line from the upper panel. Although there is considerable scatter in the data, it is seen that methane becomes progressively enriched in deuterium as the mixing ratio of CH₃D decreases. With a tropospheric CH₄ mixing ratio of (1.71±0.03)x10⁻⁶, the average δD in methane entering the stratosphere is -7(1±7)% (1σ combined precision and systematic error).

This is lower than, but within error of the ATMOS Spacelab 3 measurements of Rinsland et al. [1991] who found the average δD in methane from 18 to 28 km near latitudes of 30°N and 49°S to be -(49±44)% and -(24±25)% respectively. This is also within error of the free tropospheric measurements by Ehhalt [1973], who reported values of -86% and -94%, and Wahlen et al. [1987], who reported -80%.

**Measurement of HDO vs CH₃D and implications for HD**

In the mid to lower stratosphere, atomic H is distributed primarily among CH₄, H₂O and H₂, with negligible amounts among other species. It appears that oxidation of H₂ is roughly balanced by its production via oxidation of CH₄ through a short-lived CH₂O intermediate (Dessler et al., 1994; Abbas et al., this issue). Similarly, deuterium is most likely distributed mainly among CH₃D, HDO, and HD (with HD produced by oxidation of CH₃D and destroyed by oxidation to HDO). However, in the mid to lower stratosphere, it may not necessarily be the case that the mixing ratio of HD is as weakly varying as that of H₂. As suggested by Ehhalt et al. [1989], the lower reaction rate constant of OH and HD compared to that of OH and H₂ may serve to enrich tropospheric hydrogen gas in deuterium. However, atmospheric destruction of HD is regulated not only by rates of OH attack, but also by a large extent by those of O(1D), and the rate constant of the O(1D) reaction is not expected to be significantly affected by deuterium substitution (Kaye, 1987). (Reaction with Cl is a much more minor sink for hydrogen than for methane using the rate constants given by DeMore et al. [1994].)

For production of HD, account must be taken of not only the oxidation rates of CH₃D, but also the partitioning of D in the short-lived species in the reaction pathway from CH₃D to HD (e.g. the yield of CH₂D vs CH₃, or that of CHDO vs CH₂O). In the absence of direct measurement...
A test for changes in the HD mixing ratio is examination of those for HDO and CH$_3$D. Assuming the sum of the mixing ratios of HDO, CH$_3$D, and HD is constant, then:

$$\frac{dN(HDO)}{dN(CH$_3$D)} + \frac{dN(HD)}{dN(CH$_3$D)} = -1,$$

and any deviation of $dN(HDO)/dN(CH$_3$D)$ from -1 through the mid and lower stratosphere implies a changing mixing ratio of HD.

To compare HD and CH$_3$D mixing ratios, which are not measured simultaneously, we use the relationship in Equation 8, with $\chi = 0.84 \pm 0.02$, $\chi_{(CH}_4 = (1.71 \pm 0.03)x_{10^{-6}}$, and $\chi_{(CH)_2D} = (9.2 \pm 0.8)x_{10^{-10}}$, to estimate the CH$_3$D mixing ratio from measurements of CH$_4$. Figure 2 is a scatter plot of the HD mixing ratio in filters 2 and 9 versus this derived CH$_3$D mixing ratio. We calculate $dN(HDO)/dN(CH$_3$D)$ by a least-squares straight line fit to data where CH$_4$ mixing ratios were less than $1.4x_{10^{-6}}$ to avoid seasonal effects in HD in the lower stratosphere. The calculated slope, $-1.0x \pm 0.1$ ($1\sigma$ combined precision and systematic error), indicates that HD production is in near balance with CH$_3$D destruction. The error in the slope constrains the production of HD to be $\pm 1$ molecules HD created for each CH$_3$D molecule destroyed; however, as only about 10% of stratospheric deuterium is in HD, significant changes in the HD mixing ratio are still possible within this error. Large effects may also occur in the D/H ratio of stratospheric molecular hydrogen, but this would also be dependent on even minor changes in the H$_2$ mixing ratio due to H$_2$ photolysis or CH$_4$ oxidation (see, for example, Dessler et al. [1994]). The results in this report provide constraints for changes in HD below about 10 mb. To illustrate this, we assume a constant H$_2$ mixing ratio of $0.5x_{10^{-6}}$ and a $5D$ in hydrogen entering the stratosphere of $+(70 \pm 30)\%$ [Friedman and Scholz, 1974], which gives an initial HD mixing ratio of $(1.67 \pm 0.05)x_{10^{-10}}$. Assuming that CH$_3$D enters the stratosphere at a mixing ratio of $9.9x_{10^{-10}}$, then results here indicate that for each 1% decrease in the CH$_3$D mixing ratio, the percentage change in the HD mixing ratio from its tropospheric value is constrained to be $\pm 0.6\%$ and the change in $5D$ in molecular hydrogen can be constrained to $\pm 6\%$ ($1\sigma$).

Conclusions

We have analyzed ATMOS spectra for mid to lower stratospheric HD and CH$_3$D mixing ratios. The average D/H ratio in methane entering the stratosphere was found to be $-(71 \pm 74)\%$, but as the lifetime for CH$_3$D is greater than that of CH$_4$ by a factor of $(1.9 \pm 0.02)$, this D/H ratio increases as methane becomes oxidized. Stratospheric production of HD is $(1.0 \pm 0.1)$ times that of CH$_3$D loss, and assuming deuterated species other than HD, CH$_3$D and HD are in negligible abundance, changes in HD abundance are thus constrained to be $\pm 1$ molecules HD per molecule CH$_3$D destroyed ($1\sigma$ combined precision and systematic error). To better understand these phenomena, research is warranted into the partitioning of deuterium in CH$_3$D destruction products (including a comparison of the photolysis rates of CHDO vs that of CH$_3$O), and direct stratospheric measurements of the HD mixing ratio.

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