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Heavy hydrogen in the stratosphere

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Abstract

We report measurements of the deuterium content of molecular hydrogen (H_2) obtained from a suite of air samples that were collected during a stratospheric balloon flight between 12 and 33 km at 40° N in October 2002. Strong deuterium enrichments of up to 400‰ versus Vienna Standard Mean Ocean Water (VSMOW) are observed, while the H_2 mixing ratio remains virtually constant. Thus, as hydrogen is processed through the H_2 reservoir, deuterium is accumulated in H_2. Using box model calculations we investigated the effects of H_2 sources and sinks on the stratospheric enrichments. Results show that considerable isotope enrichments in the production of H_2 from CH_4 must take place, i.e., deuterium is transferred preferentially to H_2 during the CH_4 oxidation sequence. This supports recent conclusions from tropospheric H_2 isotope measurements which show that H_2 produced photochemically from CH_4 and non-methane hydrocarbons must be enriched in deuterium to balance the tropospheric hydrogen isotope budget. In the absence of further data on isotope fractionations in the individual reaction steps of the CH_4 oxidation sequence, this effect cannot be investigated further at present. Our measurements imply that molecular hydrogen has to be taken into account when the hydrogen isotope budget in the stratosphere is investigated.

1. Introduction

Molecular hydrogen (H_2), methane (CH_4) and water vapor (H_2O) are the three main hydrogen reservoirs in the stratosphere. Once an air parcel has entered the stratosphere, hydrogen can only be cycled between these species, since there are no net sources or sinks of hydrogen. Thus, the total hydrogen content $\chi(\hat{H}_2)=2\chi(CH_4)+\chi(H_2)+\chi(H_2O)$, where χ denotes the mixing ratio, is generally constant in the stratosphere. Significant redistribution of total hydrogen can only occur during major dehydration events, which are very rare. During these events, ice crystals grow sufficiently large to fall to lower altitudes, where they evaporate again.

Among the three stratospheric hydrogen reservoirs, H_2 is known to show virtually no changes in its mixing ratio in the stratosphere up to 40 km (Ehhalt et al., 1977). It is not that H_2 does not participate in the photochemical hydrogen cycling, but its production and loss rates are virtually identical. In the stratosphere, the most significant in situ source of H_2 is CH_4 oxidation (Fig. 1). Several reaction steps lead to the production of formaldehyde (HCHO), from which H_2 can be formed by photolysis. Figure 1 also shows that at the most 2 of the 4 hydrogen atoms in a methane molecule can finally end up in H_2. One H atom is lost in the initial abstraction reaction, a second one in the reaction step $CH_3O + O_2 \rightarrow HCHO + HO_2$. The fraction of the remaining two H atoms that form H_2 through HCHO photolysis is dependent on the relative strengths of HCHO oxidation vs. photolysis and on the relative strength of the two photolysis channels. The main stratospheric sinks of H_2 are reaction with OH and $O(^1D)$ radicals. Reaction with Cl is a minor sink.

The end product of both the CH_4 and the H_2 oxidation chains is H_2O. This means that changes in atmospheric mixing ratios of both CH_4 and H_2 have a potential impact on water vapor concentrations in the stratosphere. It is known that the tropospheric increase in CH_4 mixing ratios, which is well documented (Blake and Rowland, 1988; Etheridge et al., 1992; Dlugokencky et al., 1998), has caused an increase in stratospheric water levels (Oltmans and Hofmann, 1995; Engel et al., 1996). With H_2 being projected as a major energy carrier in the future, emissions into the atmosphere during production, storage and transport of H_2 are likely to increase (Tromp et al., 2003). This could cause a substantial increase in stratospheric H_2O levels with severe implications for the energy balance of the earth (Forster and Shine, 2002), stratospheric temperatures (Forster and Shine, 2002), microphysical conditions in the stratosphere (Tromp et al., 2003) and stratospheric ozone levels (Evans et al., 1998).

Since the H_2 mixing ratio in the lower and middle stratosphere is nearly constant, the net hydrogen cycling in the stratosphere can be regarded as a loss in methane and a production of water. Therefore, molecular hydrogen is not included in many studies that examine possible changes in the stratospheric hydrogen budget. However, during the stratospheric processing of H_2 the isotopic composition may change although mixing ratios stay constant. This is particularly true for cycling between the three stratospheric hydrogen reservoirs, since their isotopic composition is very distinct. Water vapor, on its way from the surface to the tropopause, loses heavy isotopes in condensation processes and becomes depleted in heavy isotopes. Several studies now indicate that water enters the stratosphere with an approximate isotopic composition of δD ~ −670‰ (Kuang et al., 2003). CH_4 and H_2 enter the stratosphere with their typical average tropospheric δ values of $\delta D(CH_4) \sim -86‰$ (Quay et al., 1999) and $\delta D(H_2) \sim 130‰$ (Gerst and Quay, 2000; Rahn et al., 2002b). Since both CH_4 and H_2 are strongly enriched in D compared to H_2O, it is expected that H_2O formed via oxidation of these two gases will be enriched relative to the water that enters from the troposphere. Therefore the deuterium content of stratospheric H_2O should increase as its concentration increases. Similarly, one might intuitively expect that H_2 formed from CH_4 should be isotopically light, because the CH_4 is depleted in D relative to H_2. In addition, a kinetic isotope effect in the CH_4 sink further depletes the CH_4 that is removed (see below). On the other hand, a similarly strong fractionation in the removal of H_2 by OH (HH is removed preferentially) enriches the remaining fraction of H_2. Additional isotope effects are expected in the oxidation pathway (Gerst and Quay, 2001). The net effect on the deuterium content of H_2 in the stratosphere is hard to estimate, because of the large differences in δ values between the hydrogen reservoirs and the kinetic fractionations involved. A first attempt to constrain the isotopic composition of stratospheric H_2 from combined spectroscopic deuterium measurements on stratospheric water and methane (Irion et al., 1996), did not yield detailed information on $\delta D(H_2)$.

In this paper we show that the heavy isotope content of molecular hydrogen is increasing with altitude in the stratosphere. The enrichment is surprisingly high with values reaching up to 400‰, and it correlates linearly with decreasing mixing ratios of methane.

2. Experimental

Mixing and isotope ratios of hydrogen (and a suite of other trace gases like CH_4 and N_2O) were determined from whole air samples collected cryogenically during a stratospheric balloon flight. Details of the sampler are given in Schmidt et al. (1987). Although H_2 does not condense at liquid Neon temperature, at which samples are collected, it enters the sampler entrained with the whole air flow and then cannot escape against the inflowing air under high flow conditions.

The deuterium content of H_2 is measured by continuous-flow isotope ratio mass spectrometry (CF-IRMS) using a method that has been recently developed. Details of the method will be presented elsewhere (Rhee et al. manuscript in preparation), and here we describe it in brief. An aliquot of an air sample is condensed onto the cold head (∼40 K) of a liquid Helium compressor. H_2 does not condense at that temperature (neither do He and Ne) and is subsequently flushed with a slow flow of Helium onto a cryogenic trap filled with molecular sieve. The temperature of the liquid nitrogen coolant is reduced by pumping on the head space. When the sample has been collected, it is transferred to a cryo-focus trap immersed in liquid nitrogen at the head of a molecular sieve capillary gas chromatography column. The hydrogen is then released onto the column and admitted to the mass spectrometer via an open split interface. The reproducibility of the isotope ratio measurement is presently about ±3‰, as determined from multiple measurements of a laboratory reference gas. The accuracy was checked with commercial isotope standards (IsoTop, Messer Griesheim) with nominal isotope values of −9.5‰ and +205‰ and one reference gas whose isotopic ratio was determined by conventional dual inlet IRMS.

In addition to the D/H isotope ratio, H_2 mixing ratios can be readily obtained from the combined peak areas of the two isotopologues. Results show good agreement with measurements carried out with a mercury oxide H_2 detector (T. Wetter, personal communication).

Trace gas mixing ratios are reported in nmol/mol (10^{-9}). The isotopic composition is expressed in δ notation as the relative deviation of the D/H ratio in a sample (SA) from a standard (ST), $\delta = ((D/H)_{SA}/(D/H)_{ST}-1)*1000‰$. The international standard for hydrogen isotopes is Vienna Standard Mean Ocean Water (VSMOW) with an absolute D/H ratio of $(155.76\pm0.05)\cdot10^{-6}$ (Hagemann et al., 1970). Kinetic fractionation factors in chemical reactions are expressed as the reaction rate of the heavy isotopologue relative to the light isotopologue, e.g., $\alpha_{HD-sink} = k(HD-removal)/k(HH-removal)$.

3. Results

The altitude profile of the mixing ratio of H_2 and its deuterium content determined from 13 air samples collected between 12 and 33 km over Aire sur l'Ardour, southern France (43.7° N, 0.3° W) on 24 October 2002 is shown in Fig. 2. It is known from previous studies (Ehhalt et al., 1977), that the H_2 mixing ratio does not exhibit large variations throughout this altitude range. Its δD value, however, shows a pronounced increase from typical tropospheric values of about 130‰ at 12 km to nearly 400‰ at 32.4 km. Despite the fact that H_2 is produced in the stratosphere from isotopically much more depleted CH_4, it becomes actually strongly enriched. High stratospheric $\delta D(H_2)$ values have also been recently found by Rahn et al. (2002a).

Figure 3 shows $\delta D(H_2)$ plotted versus the CH_4 mixing ratio, which is a proxy for the degree of photochemical processing in the stratosphere. It is evident that hydrogen gets progressively enriched in deuterium as CH_4 is destroyed further. The two parameters show a very compact linear correlation (R^2=0.998). We note, however, that this does not necessarily imply a chemical connection. When we compare any two stratospheric species with local life times that are substantially longer than the transport times, their distribution is dominated by transport processes rather than chemistry, which does result in compact correlations (Plumb and Ko, 1992). We note that since this is true for both H_2 and CH_4 (Zöger et al., 1999), the relation presented in Fig. 3 is not only characteristic for this single time and location, but is expected to hold (with possible small variations) throughout large regions of the stratosphere.

4. Discussion

The strong isotope enrichments convincingly illustrate that H_2 is not a mere spectator of stratospheric hydrogen cycling, but it plays an active role. Although the H_2 mixing ratio is constant, there must be a continuous production and destruction of H_2 to cause the observed deuterium enrichment. If we assume that the general understanding of hydrogen sources and sinks in the stratosphere is correct, this can only be due to either a faster production of HD compared to HH from CH_4 oxidation, or a preferential destruction of HH, or both.

In their investigation of the tropospheric hydrogen budget, Gerst and Quay (2001) have investigated this issue in detail in an endeavor to explain the high δD value of H_2 in the troposphere. We will discuss our stratospheric data along the same lines, but for stratospheric conditions. The fractionation in the stratospheric H_2 sinks can be quantified, since fractionation constants have been determined experimentally. The situation is less favorable for the stratospheric H_2 source, i.e., production of H_2 from CH_4. Fractionations of large magnitude are expected to occur in several reaction steps along the reaction sequence (Fig. 1) (Gerst and Quay, 2001). Unfortunately, quantitative information is lacking for most of them, and it is not yet possible to model the transfer of deuterium through the CH_4 oxidation chain. Therefore, at this stage we do not investigate the individual reaction steps and only attempt to answer the question: What isotopic composition is required for H_2 produced by CH_4 oxidation to explain the stratospheric observations? In the following, we name this quantity $\delta D(H_2)_{\text{source}}$ since photochemically produced H_2 is the only molecular hydrogen source in the stratosphere. The aim is to determine a value for $\delta D(H_2)_{\text{source}}$ which leads to a $\delta D(H_2){-}CH_4$ correlation as shown in Fig. 3. A similar approach was also adopted from Gerst and Quay (2001). In their study, however, the situation was different due to the unknown relative strengths of the photochemical and the soil sinks in the troposphere. In the stratosphere, only photochemistry is important.

We carry out box model calculations to illustrate the relevant fractionation effects in our simplified system. At the outset, we want to mention the limitations of using a box model for this purpose. They arise primarily due to the fact that a box model does not include effects of diffusion, transport and mixing. It has been shown, however, that these dynamical processes affect the isotopic composition of long-lived stratospheric trace gases, which are removed in the stratosphere (Röckmann et al., 2001; Kaiser et al., 2002). Generally, the ”apparent” fractionation constants which can be derived from stratospheric observations are significantly lower than the kinetic fractionation constants determined in the chemical removal reactions in the laboratory (Appendix A). This is taken into account by using the apparent fractionation constants rather than the actual kinetic fractionation constants in the box model. Whereas this approach leads to realistic magnitudes of the isotope fractionation in box models, mixing is of course not treated realistically this way, because in reality mixing affects the isotope ratios by smoothing out gradients. This means that a modeled vertical profile may still include additional structure, e.g. a curvature, which is not sufficiently ”smeared out”, due to the inadequate way of including dynamical effects (in particular for the case of H_2 which also has a stratospheric source). Thus, reliable detailed altitude profiles can only be expected from at least 1D modeling with a realistic parameterization of vertical mixing. Knowing about these limitations, we perform the following box model calculations to illustrate the individual fractionation mechanisms and to put some constraints on the isotopic composition of H_2 produced from CH_4 oxidation.

In our model, the starting point is always an air parcel entering the stratosphere with 1750 nmol/mol CH_4, 500 nmol/mol H_2 and $\delta D(H_2)=130‰$. The isotopic composition of CH_4 is irrelevant since we are only interested in the final product, i.e., $\delta D(H_2)_{source}$. At each model step, a small fraction of CH_4 is removed, and H_2 is produced with a certain yield y and isotopic composition $\delta D(H_2)_{source}$. To keep the H_2 mixing ratio constant, the same amount of H_2 is then removed again with the relevant fractionation constant $\alpha_{HD-sink}$. Figure 4a illustrates the approach for a simple example. In the first box model run (green lines), H_2 is produced with $\delta D(H_2)_{source}=-80‰$, which is the isotopic composition of tropospheric CH_4, the initial source material. Fractionations in H_2 sinks are not included ($\alpha_{HD-sink}$=1), thus δD(H$_2$)$_{source}$ does not change as methane mixing ratios decrease. Light hydrogen is thus transferred to the H$_2$ reservoir and causes a considerable depletion although the mixing ratio is constant. The extent of hydrogen transfer depends on the fraction of hydrogen that is processed via H$_2$, and we assume two cases for the H$_2$ yield from CH$_4$ oxidation, y=0.6 and y=1.0, i.e., for each CH$_4$ molecule destroyed 0.6 and 1 H$_2$ molecules are formed, respectively. As expected, when lesshydrogen is processed via H$_2$ (y=0.6), the transfer is smaller.

In the second step, fractionations in the H$_2$ sinks are included. $\alpha_{HD-sink}$=0.76 is an estimate for a globally weighted average of the fractionations in the two sink reactions with OH and O(^{1}D) (Appendix A), and $\alpha_{HD-sink,app}$=0.854 is the apparent fractionation factor to be expected in the stratosphere under the influence of diffusive mixing (Appendix A). The substantial isotope fractionation in the removal of H$_2$ does lead to an appreciable enrichment in the remaining H$_2$ fraction. Nevertheless, Figure 4a shows that the effect of the sink alone does not lead to the observed enrichments. Calculations are shown again for a H$_2$ yield of y= 0.6 and y=1.0. As shown in Appendix A, α_{app} is considered more realistic for the stratosphere (close to diffusion limited case), and we use this value as well as y=1.0 in the following.

The final parameter used in the model is the change of δD(H$_2$)$_{source}$ with altitude. Since δD(H$_2$)$_{source}$ does originate from CH$_4$, changes in the δD(CH$_4$) value lead to changes in δD(H$_2$)$_{source}$. The change of δD(CH$_4$) with CH$_4$ mixing ratio in the stratosphere can be predicted from the relative ^{13}C and D fractionation constants for the sink reactions, observations of δ^{13}C(CH$_4$) changes as a function of CH$_4$ mixing ratio and results from 2D modeling that are in good agreement with the observations for δ^{13}C(CH$_4$). As shown in Appendix A, $\alpha_{CH_3D-sink,app}$ = 0.865 should be a realistic apparent fractionation constant taking into account diffusive mixing, with the limitations as discussed above.

Assuming initially a constant relationship between the CH$_4$ source material and the H$_2$ product in the stratosphere, we parameterize the change of δD(H$_2$)$_{source}$ with decreasing methane mixing ratio by the parameter $\alpha_{CH_3D-sink,app}$. Thus, δD(H$_2$)$_{source}$ increases with decreasing CH_4 mixing ratio (Fig. 4b), which leads to higher stratospheric $\delta D(H_2)$ values at smaller CH_4 mixing ratios. Parametrizing the change of $\delta D(H_2)_{source}$ with altitude by $\alpha_{CH_3D-sink,app}$ also means that the choice of $\delta D(H_2)_{source}$ is only free at the tropopause, and we will denote this value $\delta D(H_2)_{s0}$. This is the value that we try to constrain in the following from our observations.

The model is thus characterized by three parameters, namely $\alpha_{HD-sink,app}$, $\alpha_{CH_3D-sink,app}$, and $\delta D(H_2)_{s0}$, but clearly the values chosen above cannot explain the stratospheric observations. Gerst and Quay (2001) concluded from tropospheric H_2 isotope budget considerations that $\delta D(H_2)_{source}$ should be (130±70)‰ in the troposphere to explain the high tropospheric $\delta D(H_2)$ value. If $\delta D(H_2)_{s0}$=130‰ is used in the model, the resulting enrichments are closer to, but still lower than the observations (Fig. 4c). Figure 4d shows that keeping the other parameters constant, the high stratospheric enrichments can be modeled fairly well using $\delta D(H_2)_{s0} \approx 190 \pm 40$‰.

In the following, the other parameters of the model are varied. In Fig. 4e, $\alpha_{HD-sink,app}$ is changed from the value adopted above (0.854) in three steps to 0.84, 0.8 and finally to the value in the reaction limit (0.76). This is a huge change, and most likely unrealistic, as argued in Appendix A. Comparing Fig. 4e to d shows that lowering the value of the parameter $\alpha_{HD-sink,app}$ has a similar effect as increasing $\delta D(H_2)_{s0}$. Thus, when $\alpha_{HD-sink,app}$ is decreased sufficiently the model results are in the range of the observations already for $\delta D(H_2)_{s0}$=130‰.

In Fig. 4f the change in $\delta D(H_2)_{source}$ with altitude, parameterized by the value $\alpha_{CH_3D-sink,app}$, is varied. Note again that changes in $\alpha_{CH_3D-sink,app}$ do not imply a change in the fractionation associated with CH_4 oxidation, but only characterize the product H_2. Fractionations in other individual reaction steps in the CH_4 oxidation sequence can cause an altitude dependence of $\delta D(H_2)_{source}$ that varies from the $\delta D(CH_4)$ profile. Two different values for $\alpha_{CH_3D-sink,app}$ are chosen, 0.78, the value under reaction limited conditions and an even lower value of 0.68. $\delta D(H_2)_{s0}$ is adjusted again to yield results close to the measurements. In these runs parameters are chosen such that $\delta D(H_2)_{source}$ varies much more strongly with altitude (Fig. 4f). Interestingly, the curvature in the modeled stratospheric profile disappears, which indicates that it strongly depends on the isotopic composition of the H_2 source. In fact, a good agreement of the modeled $\delta D(H_2)$ profile and the data is obtained if the profiles of $\delta D(H_2)_{source}$ and $\delta D(H_2)$ are rather similar. As explained above, precise agreement between the altitude profile of our box model runs and the observations is not expected, due to the fact that stratospheric mixing is only taken into account by adjusting the fractionation constants. In reality we expect mixing processes to remove some of the curvature seen in the calculated correlations.

Regarding the value of $\delta D(H_2)_{s0}$ the model calculations show a quite consistent picture. Including all the sensitivity tests, which cover a large range, values of $\delta D(H_2)_{s0}$ between 130‰ and 230‰ are required to reproduce the stratospheric observations. If we assume that $\delta D(H_2)_{s0}$, the deuterium content of H_2 produced from CH_4 near the tropopause is similar to $\delta D(H_2)_{source}$ for the troposphere, then this range can also be adopted for the troposphere. Thus, the stratospheric data constrain the range of (130±70)‰ for photochemically produced H_2 predicted by Gerst and Quay (2001) based on tropospheric H_2 budget calculations to the upper half. A reduction of the range of the deuterium content of photochemically produced H_2 by a factor of two puts a major constraint on the global H_2 budget (Gerst and Quay, 2001).

The range of 130 to 230‰ for $\delta D(H_2)_{s0}$ as derived in the box model runs indicates that an overall isotope enrichment of roughly 240 to 350‰ occurs in the oxidation sequence from CH_4 with $\delta D(CH_4) \sim -86‰$ to the final H_2 product (note that δ values do not add linearly). This massive enrichment must originate from one or more individual reaction steps in the CH_4 oxidation sequence (Fig. 1). Unfortunately, little quantitative information about the individual reaction steps is available, which prevents a detailed investigation at present. As discussed in Gerst and Quay, (2001), at least in the initial hydrogen abstraction step of the CH_4 oxidation sequence (Fig. 1), H is expected to be removed preferentially, which would cause a deuterium enrichment in the final reaction product H_2. For more details the reader is referred to Gerst and Quay (2001), where all available isotope information about the reaction sequence is provided.

5. Conclusions

High precision δD measurements on stratospheric H_2 reveal a pronounced deuterium enrichment that increases with degree of photochemical processing in the stratosphere. An approximately linear relationship between $\delta D(H_2)$ and CH_4 concentration is found with δD values increasing from 130‰ near the tropopause up to 400‰ at CH_4 mixing ratios of 900 nmol/mol. The deuterium enrichments demonstrate that stratospheric molecular hydrogen plays an important role in the stratospheric deuterium budget and has to be included in global budget calculations. Box model calculations show that to explain the enrichment, H_2 produced from CH_4 oxidation must be strongly enriched vs. the CH_4 source material, in agreement with conclusions from tropospheric measurements (Gerst and Quay, 2001), and the value near the tropopause can be tightly constrained to $\delta D(H_2)_{s0}=(180\pm50)$‰.

Appendix A: Fractionation constants in the stratosphere

The two major sinks of H_2 in the stratosphere are reaction with OH and $O(^1D)$, with only a minor contribution from Cl (LeTexier et al., 1988). The relevant isotope effects have been determined and are listed in Table 1. Whereas there is no kinetic fractionation in the reaction $O(^1D) + H_2$, the reaction OH + H_2 proceeds almost twice as fast as OH + HD at typical stratospheric temperatures of 230 K. The global average stratospheric removal rate of H_2 by OH is similar to that by $O(^1D)$ (LeTexier et al., 1988). Thus the globally averaged kinetic fractionation factor is the average of the two individual fractionation factors, thus $\alpha_{\text{HD-sink}} \approx 0.76$.

In the stratosphere, CH_4 is removed by the three radicals OH, $O(^1D)$ and Cl. The relevant reactions have been characterized isotopically (Saueressig et al., 1996; Saueressig et al., 2001). Table 2 lists the fractionation constants for stratospheric temperatures. All oxidants preferentially remove light CH_4, and the remaining methane gets enriched. The relative shares of the three removal reactions can be obtained from recent model calculations of stratospheric CH_4 isotope ratios (Bergamaschi et al., 1996; Saueressig et al., 2001). Since there are no high precision measurements of δD in CH_4 available yet, constraints for models thus far come from $\delta^{13}C(CH_4)$. The model used by Saueressig et al. (2001) found a good match with observations (Sugawara et al., 1997) for global average removal rates of 41% oxidation by OH, 31% oxidation by $O(^1D)$ and 28% oxidation by Cl (C. Brühl, pers. comm.). A large set of new measurements (M. Braß et al., manuscript in preparation) confirms these numbers. The weighted global average fractionation constant for H abstraction from CH_4 is thus $\alpha_{CH_3D-sink} = 0.78$.

However, due to the effects of diffusion and mixing, the apparent (i.e. observed) fractionation factors α_{app} in the stratosphere are significantly smaller than the ones of the removal reactions themselves (Röckmann et al., 2001). This has been supported theoretically by Kaiser et al. (2002), who showed that α_{app} ranges from α in the reaction limited case to $\sqrt{\alpha}$ in the diffusion limited case. Also, mixing of air masses with different isotopic composition decreases the apparent fractionations.

A comparison of reaction rate constants calculated by the 2D model (C. Brühl, pers. comm.) and vertical eddy diffusion coefficients (Froidevaux and Yung, 1982) indicates that the stratospheric situation is in between the pure diffusion limited and reaction limited cases. Thus, to estimate suitable apparent fractionation constants we use the comparison of available laboratory fractionation data and stratospheric measurements. Comparison of laboratory and stratospheric isotope measurements for N_2O (Röckmann et al., 2001) demonstrate that we are close to the diffusion limited case in the lower and middle stratosphere. Also $\delta^{13}C(CH_4)$ measurements show that the apparent fractionation factor $\alpha_{13CH_4-sink,app} \approx 0.985$ (Sugawara et al., 1997) is significantly larger than $\alpha_{13CH_4-sink} \approx 0.975$, the removal rate weighted fractionation constant for the three sinks, and close to $\sqrt{\alpha_{13CH_4-sink}} = 0.987$, the value under diffusion limited conditions. In Table 3, our best estimates for stratospheric apparent fractionation constants in the removal reactions of CH_4 and H_2 are shown. They are closer to the diffusion limited value, based on the observations of $\delta^{13}C$ in CH_4. These numbers are used as starting values in the box model calculations presented in this paper. We note that, in the absence of experimental data, at this point we do not include in the model potential variations of the apparent fractionation factors with altitude, which may arise due to altitudinal variations in the removal rates of H_2 and CH_4 by the individual radical reactions.

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Table 1. Rate coefficients (in cm^{3}molecule^{-1}s^{-1}) for the reaction of H_2 and HD with O(^{1}D) and OH for stratospherically relevant temperatures from (Talukdar et al., 1996; Talukdar and Ravishankara, 1996) and the corresponding fractionation factors

	k(230 K)	α(230 K)
O(^{1}D) + H_2	1.1×10^{-10}	
O(^{1}D) + HD	1.1×10^{-10}	1.00
OH + H_2	9.2×10^{-16}	
OH + HD	4.75×10^{-16}	0.52

Table 2. Fractionation constant for the CH_4 removal reactions from (Saueressig et al., 2001), globally averaged removal strengths for the different radicals derived from model calculations (C. Brühl, pers. comm.), and the calculated globally averaged fractionation constant

reactant	share of total removal	α(230 K)
OH	41%	0.735
$O(^1D)$	32%	0.943
Cl	28%	0.626
global average $\alpha_{CH_3D-sink}$		0.778

Table 3. Global average fractionation constants for the removal of CH_4 and H_2 in reaction limited conditions (α), diffusion limited conditions ($\sqrt{\alpha}$), and the best estimate for a realistic α_{app} in the stratosphere

	α	$\sqrt{\alpha}$	α_{app}
H_2 sink	0.76	0.872	0.854
CH_4 sink	0.778	0.882	0.865

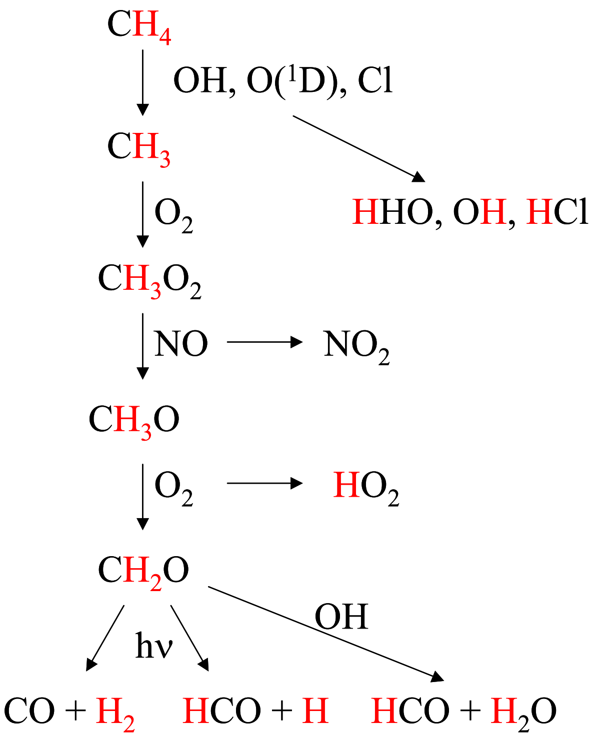

Fig. 1. Schematic diagram of the CH_4 oxidation pathway that leads to H_2 production. Out of the 4 hydrogen atoms initially present (marked in red), two end up in H_2CO and are available for transfer into H_2. The other two are transferred to other reaction products and eventually end up as water. In particular in these hydrogen abstraction steps large fractionations can occur if H is preferentially removed.

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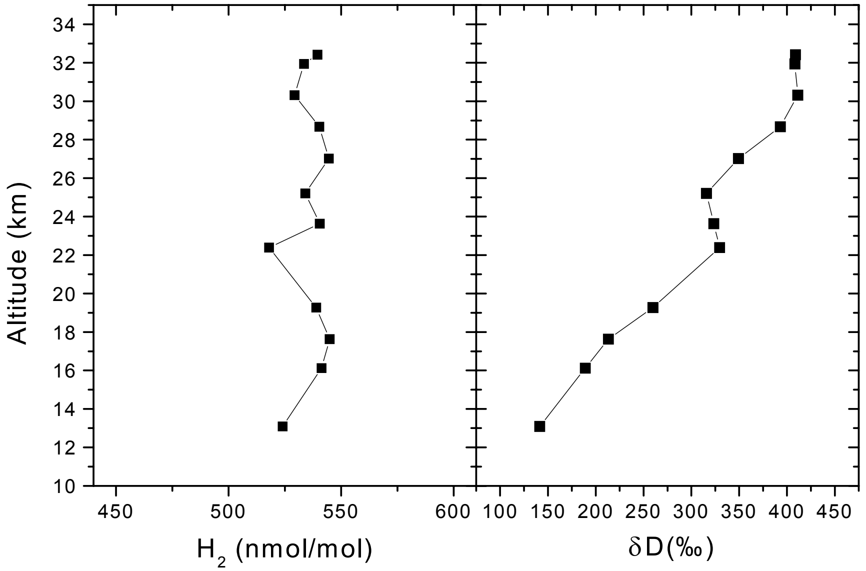

Fig. 2. Hydrogen mixing ratio and δD(H_2) in the stratosphere as a function of altitude. Although the mixing ratio stays virtually constant, δD(H_2) increases almost 300‰.

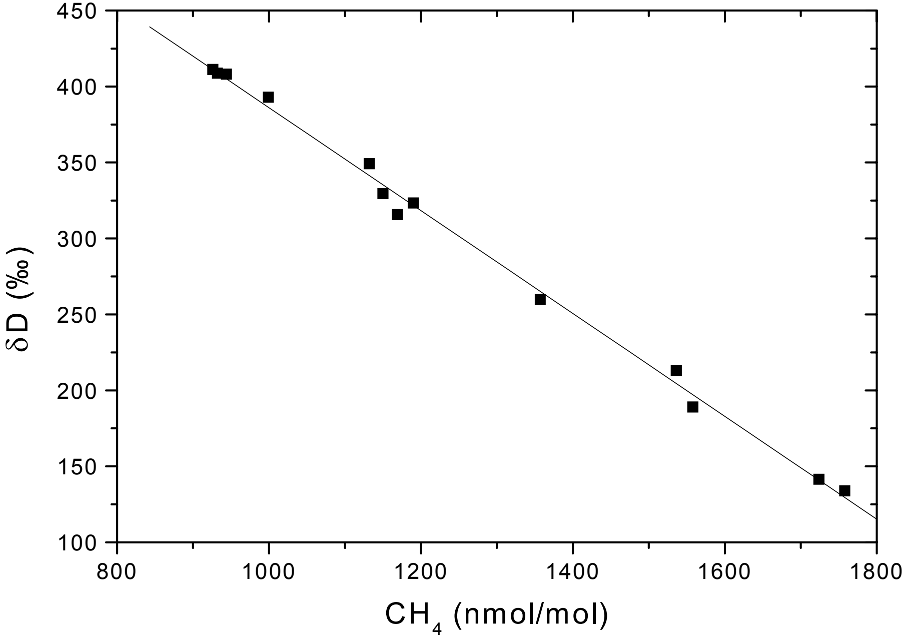

Fig. 3. δD(H_2) plotted versus CH_4 mixing ratio, which was independently determined on the samples by Marc Braß (manuscript in preparation) with errors of ∼1%.

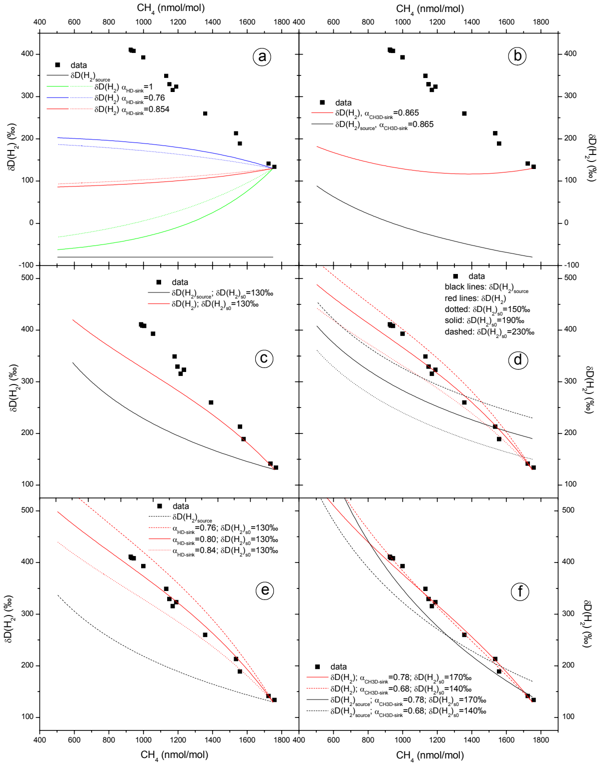

Fig. 4. Caption on next page. For detail use zoom tool.

Fig. 4. Box model calculation results illustrating the effects of fractionation in hydrogen sources and sinks **(a)–(c)** and the sensitivity to the individual parameters **(d)–(f)**. δD is plotted as a function of CH_4 mixing ratio. (a) includes only the fractionation in the H_2 removal reactions for three different fractionation constants $\alpha_{HD-sink}$ and for H_2 yields from CH_4 of y=1.0 (molec H_2/molec CH_4 removed), solid lines, and y=0.6 (molec H_2/molec CH_4 removed), dotted lines. In (b) the change of $\delta D(H_2)_{source}$ with CH_4 mixing ratio, parameterized by $\alpha_{CH_3D-sink,app} = 0.865$, is added. This leads to an enrichment of $\delta D(H_2)_{source}$ with decreasing concentration. In (c) $\delta D(H_2)_{s0}$=130‰ from Gerst and Quay is used, but even higher values of $\delta D(H_2)_{s0}$=150‰ to 230‰ (d) are necessary to bring the model results to the range of the observations. In (e) the fractionation factor for the H_2 sink, $\alpha_{HD-sink,app}$ is varied, in (f) $\alpha_{CH_3D-sink,app}$ is varied. $\delta D(H_2)_{s0}$ is always adjusted to yield results that are in agreement with the observations.