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# Modelling the budget of middle atmospheric water vapour isotopes

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**Abstract.** A one-dimensional chemistry model is applied to study the stable hydrogen (D) and stable oxygen isotope ( $^{17}\text{O}$ ,  $^{18}\text{O}$ ) composition of water vapour in stratosphere and mesosphere. In the troposphere, this isotope composition is determined by “physical” fractionation effects, that are phase changes (e.g. during cloud formation), diffusion processes (e.g. during evaporation from the ocean), and mixing of air masses. Due to these processes water vapour entering the stratosphere first shows isotope depletions in D/H relative to ocean water, which are  $\sim 5$  times of those in  $^{18}\text{O}/^{16}\text{O}$ , and secondly is mass-dependently fractionated (MDF), i.e. changes in the isotope ratio  $^{17}\text{O}/^{16}\text{O}$  are  $\sim 0.52$  times of those of  $^{18}\text{O}/^{16}\text{O}$ . In contrast, in the stratosphere and mesosphere “chemical” fractionation mechanisms, that are the production of  $\text{H}_2\text{O}$  due to the oxidation of methane, re-cycling of  $\text{H}_2\text{O}$  via the  $\text{HO}_x$  family, and isotope exchange reactions considerably enhance the isotope ratios in the water vapour imported from the troposphere. The model reasonably predicts overall enhancements of the stable isotope ratios in  $\text{H}_2\text{O}$  by up to  $\sim 25\%$  for D/H,  $\sim 8.5\%$  for  $^{17}\text{O}/^{16}\text{O}$ , and  $\sim 14\%$  for  $^{18}\text{O}/^{16}\text{O}$  in the mesosphere relative to the tropopause values. The  $^{17}\text{O}/^{16}\text{O}$  and  $^{18}\text{O}/^{16}\text{O}$  ratios in  $\text{H}_2\text{O}$  are shown to be a measure of the relative fractions of  $\text{HO}_x$  that receive the O atom either from the reservoirs  $\text{O}_2$  or  $\text{O}_3$ . Throughout the middle atmosphere, MDF  $\text{O}_2$  is the major donor of oxygen atoms incorporated in OH and  $\text{HO}_2$  and thus in  $\text{H}_2\text{O}$ . In the stratosphere the known mass-independent fractionation (MIF) signal in  $\text{O}_3$  is in a first step transferred to the  $\text{NO}_x$  family and only in a second step to  $\text{HO}_x$  and  $\text{H}_2\text{O}$ . In contrast to  $\text{CO}_2$ ,  $\text{O}(^1\text{D})$  only plays a minor role in this MIF transfer. The major uncertainty in our calculation arises from poorly quantified isotope exchange reaction rate coefficients and kinetic isotope fractionation factors.

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## 1 Introduction

Water vapour ( $\text{H}_2\text{O}$ ) belongs to the most important trace gases in the Earth’s atmosphere. It plays a key role for numerous homogeneous and heterogeneous chemical reactions (Lelieveld and Crutzen, 1990, 1994) as well as for the short-wave and long-wave radiative budget of the atmosphere (IPCC, 2001). Its extremely complex atmospheric cycle is not understood in sufficient detail, in particular since atmospheric water is present in the gaseous, liquid, and solid phase.

The interest in middle atmospheric  $\text{H}_2\text{O}$  was further intensified following observations made by Oltmans and Hofmann (1995) and after this by others (SPARC, 2000, and references therein; Rosenlof et al., 2001) who found increasing  $\text{H}_2\text{O}$  concentrations of 30–150 nmol/mol  $\text{yr}^{-1}$  in the middle atmosphere since 1954. Not only the possible causes of this trend but also the consequences for Earth’s climate and the chemistry of the middle atmosphere are a matter of vital discussion (Forster and Shine, 1999, 2002; Kirk-Davidoff et al., 1999; Stenke and Grewe, 2004; Röckmann et al., 2004).

To date primarily  $\text{H}_2\text{O}$  concentration measurements, supported by atmospheric circulation models, have been used to place constraints on the hydrological cycle in the middle atmosphere (Dessler et al., 1995; Rosenlof et al., 1997; Randel et al., 2001). Independent information can be gained from the analysis of the isotopic composition of water vapour.

The isotope ratios in water vapour are usually reported as per mil deviation of the ratio “rare isotopologue” to “most abundant isotopologue” relative to the Vienna Standard Mean Ocean Water (V-SMOW) reference, e.g.  $\delta^{18}\text{O}(\text{H}_2\text{O}) = (\text{R}_{18\text{O, sample}}/\text{R}_{18\text{O, V-SMOW}} - 1) \cdot 1000\%$ , where  $\text{R}_{18\text{O}}$  denotes the isotopologue ratio  $\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$  of a sample or V-SMOW, respectively.  $\text{R}_{\text{D, V-SMOW}}$  is  $0.31152 \cdot 10^{-3}$  (Hagemann et al., 1970; DeWit et al., 1980; Tse et al., 1980),  $\text{R}_{17\text{O, V-SMOW}}$  is  $0.3799 \cdot 10^{-3}$  (Li et al., 1988), and  $\text{R}_{18\text{O, V-SMOW}}$  is  $2.0052 \cdot 10^{-3}$  (Baertschi, 1976). All  $\delta\text{D}$ ,

$\delta^{17}\text{O}$ , and  $\delta^{18}\text{O}$  values in this paper are given with respect to V-SMOW.

The major source of atmospheric water vapour is the ocean having an isotope composition close to V-SMOW, i.e.,  $\delta^{18}\text{O}(\text{H}_2\text{O}) \approx 0\text{‰}$ . Evaporation into the atmosphere leads to depletion in the rare H<sub>2</sub>O isotopologues relative to H<sub>2</sub><sup>16</sup>O, due to their lower vapour pressure compared to H<sub>2</sub><sup>16</sup>O, the vapour pressure isotope effect (v.p.i.e.). Typically,  $\delta^{18}\text{O}(\text{H}_2\text{O})$  is  $-12\text{‰}$  and  $\delta\text{D}(\text{H}_2\text{O})$  is  $-85\text{‰}$  just above the ocean (Rozanski et al., 1993). Cooling during upward air movement causes cloud formation and (due to the v.p.i.e.) preferential condensation and subsequent removal of the rare H<sub>2</sub>O isotopologues by precipitation. The D/H, <sup>17</sup>O/<sup>16</sup>O, and <sup>18</sup>O/<sup>16</sup>O isotope ratios in H<sub>2</sub>O thus decrease with altitude and reach tropopause values in the range of  $\delta\text{D}(\text{H}_2\text{O}) \approx -(450\text{--}750)\text{‰}$ ,  $\delta^{17}\text{O}(\text{H}_2\text{O}) \approx -(30\text{--}70)\text{‰}$ , and  $\delta^{18}\text{O}(\text{H}_2\text{O}) \approx -(60\text{--}130)\text{‰}$ , respectively (see Sect. 2). This isotopically depleted water vapour is transported to the stratospheric overworld, almost exclusively within the tropics (Holton et al., 1995; Highwood and Hoskins, 1999).

There and in contrast to the troposphere, chemical reactions considerably modify the isotope composition of the water vapour imported from the troposphere such as: (i) methane (CH<sub>4</sub>) oxidation, the main in situ source of H<sub>2</sub>O in the stratosphere, (ii) exchange of oxygen atoms with molecular oxygen and ozone via the HO<sub>x</sub> and NO<sub>x</sub> family, and (iii) oxygen isotope exchange reactions e.g. between H<sub>2</sub>O and OH (Greenblatt and Howard, 1988; Masgrau et al., 1999). Importantly, all of these processes enrich the water vapour imported from the troposphere in the rare isotopes.

Using a one-dimensional (1-D) model we show in this paper, how these chemical reactions modify the stable isotope composition of middle atmospheric H<sub>2</sub>O and how H<sub>2</sub>O isotope observations may be exploited to infer constraints on these reactions and on the budget of stratospheric water. Four previous model studies on the isotopic composition of stratospheric H<sub>2</sub>O have been made. Kaye (1990) first studied  $\delta^{18}\text{O}(\text{H}_2\text{O})$  in the middle atmosphere and suggested a significant increase in  $\delta^{18}\text{O}(\text{H}_2\text{O})$  with altitude due to <sup>18</sup>O-rich excess water from CH<sub>4</sub> oxidation. Ridal et al. (2001) and Ridal (2002) focused on  $\delta\text{D}(\text{H}_2\text{O})$  in the stratosphere. They found a strong vertical increase of  $\delta\text{D}(\text{H}_2\text{O})$ , also due to CH<sub>4</sub> oxidation which is additionally modulated by the seasonally varying H<sub>2</sub>O input from the troposphere (the “tape recorder effect”). Johnson et al. (2001a) applied a simple photochemical model with many simplifications, but inferred excellent agreement with own  $\delta\text{D}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  balloon-borne observations conducted between 1989 and 1997.

The major difference of the present model study compared to earlier work is first that all three stable isotope signatures  $\delta\text{D}(\text{H}_2\text{O})$ ,  $\delta^{17}\text{O}(\text{H}_2\text{O})$ , and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  both in the stratosphere as well as in the mesosphere are combined, and second that a large number of isotope exchange reactions and all isotope fractionation coefficients measured so far are considered. Special emphasis is put on the specific pathways of D,

<sup>17</sup>O, and <sup>18</sup>O from their reservoir species CH<sub>4</sub>, H<sub>2</sub>, O<sub>2</sub>, and O<sub>3</sub> into the end product H<sub>2</sub>O.

## 2 Available stable isotope data of H<sub>2</sub>O

Due to the difficulty to measure the isotopic composition of stratospheric water with sufficient accuracy, only a limited number of H<sub>2</sub>O isotope data have been gathered so far, which are grouped in the following according to the analytical technique employed.

(i) Most stable isotope H<sub>2</sub>O data were collected using remote-sensing infrared spectroscopy techniques (Abbas et al., 1987; Carli and Park, 1988; Guo et al., 1989; Dinelli et al., 1991, 1997; Rinsland et al., 1984, 1991; Stowasser et al., 1999; Johnson et al., 2001; Kuang et al., 2003). They all reveal strong depletions of  $\delta\text{D}(\text{H}_2\text{O})$  with respect to V-SMOW which significantly decrease with altitude, from about  $-(660 \pm 80)\text{‰}$  at the tropical tropopause (Moyer et al., 1996; Johnson et al., 2001; Kuang et al., 2003; McCarthy et al., 2004) to typically  $-(450 \pm 70)\text{‰}$  at 40 km. Observations by Stowasser et al. (1999) showed extreme  $\delta\text{D}(\text{H}_2\text{O})$  depletions as low as  $-830\text{‰}$  at 17 km inside the Arctic vortex, which was attributed to condensation and subsequent sedimentation of polar stratospheric cloud (PSC) particles.

For  $\delta^{17}\text{O}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$ , most studies report values between 0 and  $-100\text{‰}$  and a weak vertical increase. However, this increase is mostly not significant due to the large measurement uncertainties of 50–120‰. In contrast, early observations by Guo et al. (1989) showed increasing  $\delta^{18}\text{O}(\text{H}_2\text{O})$  values from  $(80 \pm 140)\text{‰}$  at 22 km altitude to  $(400 \pm 250)\text{‰}$  at 37 km. Using a balloon-borne spectrometer, Johnson et al. (2001) obtained low isotope ratios of  $-(300\text{--}30)\text{‰}$  (average:  $-128\text{‰}$ ) for  $\delta^{18}\text{O}(\text{H}_2\text{O})$ , and of  $-(400\text{--}0)\text{‰}$  (average:  $-84\text{‰}$ ) for  $\delta^{17}\text{O}(\text{H}_2\text{O})$  at 12–20 km altitude.

(ii) Cryogenic in situ sampling and subsequent laboratory-based mass spectrometry (MS) analysis constitutes the potentially most accurate technique, but suffers from the very small sample amounts available and their difficult handling and MS analysis. Most observations are from the upper troposphere and lowermost stratosphere (Ehhalt, 1974; Smith, 1992; Zahn et al., 1998; Zahn, 2001) and to date there is only one set of balloon-borne stratospheric  $\delta\text{D}(\text{H}_2\text{O})$  profiles available (Pollock et al., 1980). These data likewise show a continuous increase in  $\delta\text{D}(\text{H}_2\text{O})$  with altitude, from about  $-450\text{‰}$  at 25 km to about  $-360\text{‰}$  at 35 km.

The single investigation on the oxygen ( $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) isotope composition of stratospheric H<sub>2</sub>O samples was conducted by Franz and Röckmann (2005) using samples obtained between New Zealand and Antarctica in August/October 2004 at altitudes of up to  $\sim 5$  km above the local tropopause. The data show an increase of  $\delta^{18}\text{O}$  concomitant with decreasing H<sub>2</sub>O mixing ratios above the local tropopause. This was interpreted as mixing of tropospheric and stratospheric overworld air in the high latitude

lowermost stratosphere. Notably, the data show no oxygen isotope anomaly with very small errors of  $\Delta^{17}\text{O}(\text{H}_2\text{O}) < 2\%$ .

(iii) In situ infrared laser spectroscopic techniques are challenging, potentially very accurate and may additionally offer high spatial resolution. First applications on board aircraft have been reported.

Using the tunable diode laser absorption spectrometer (TDLAS) ALIAS on board the high-flying NASA WB-57 aircraft, Webster and Heymsfield (2003) observed (expectedly) decreasing  $\delta\text{D}$ ,  $\delta^{17}\text{O}$ , and  $\delta^{18}\text{O}$  values in H<sub>2</sub>O with increasing height up to the tropical tropopause. The high temporal resolution measurement also revealed a very high degree of variability, e.g.  $\delta\text{D}$  values ranging from 0 and  $-900\%$  near the tropopause and clearly different values for ice and gas water, respectively. Surprisingly, the mean  $\delta\text{D}:\delta^{18}\text{O}$  ratio for this data set is only  $< 3$  in the lower stratosphere.

In May 2004 Kerstel, Romanini, and Jost applied a cavity-ring-down technique (off-axis cavity enhanced absorption spectroscopy, OF-CEAS) on-board a DC-10 aircraft at altitudes of up to 13 km. They reported on excellent measurement uncertainties of below 10‰ for all three stable isotopologues over a certain 10 min sampling interval with particular constant H<sub>2</sub>O mixing ratios of  $\sim 200$  ppmv (personal communication).

High measurement accuracies are reported by Keutsch et al. (Harvard University) who measured  $\delta\text{D}$  and  $\delta^{18}\text{O}$  in H<sub>2</sub>O at altitudes of up to 20 km in autumn 2004 by using off-axis integrated cavity output spectroscopy (OF-ICOS) on-board the NASA WB-57. On the same flights a photofragment laser-induced fluorescence (LIF) technique were applied for measuring  $\delta\text{D}$  in H<sub>2</sub>O by Hanisco et al. (Harvard University) with similarly low measurement uncertainty.

### 3 Information provided by the H<sub>2</sub>O isotopic composition

The isotopic composition of tropospheric water vapour is controlled by the hydrological cycle. Hence, H<sub>2</sub>O isotope data can be used as tracers for the condensation history of probed air masses (Taylor, 1984), e.g. for studying the transport of tropospheric H<sub>2</sub>O into the lowermost stratosphere (Zahn, 2001).

Both,  $\delta\text{D}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  are primarily determined by the v.p.i.e. (see Sect. 1) and thus undergo similar variations. Indeed, in surface precipitation both isotopologues are closely related by the meteoric water line (MWL):  $\delta\text{D}(\text{H}_2\text{O}) \approx m \times \delta^{18}\text{O}(\text{H}_2\text{O}) + 10\%$ , with  $m \approx 8$  (Craig, 1961). This relationship was found to hold reasonably well even on Mount Logan (Canada) at 5951 m altitude, with  $m = 7.5$  (Holdsworth et al., 1991). At cold temperatures as encountered in the tropical tropopause layer (TTL), however, kinetic isotope fractionation during formation of ice cloud particles, their lofting in convective cells and mixing of air masses with different H<sub>2</sub>O isotope compositions are assumed to consid-

erably reduce  $\delta\text{D}(\text{H}_2\text{O})$  depletion compared to  $\delta^{18}\text{O}(\text{H}_2\text{O})$  (Moyer et al., 1996; Keith, 2000; Johnson et al., 2001; Kuang et al., 2003; Dessler and Sherwood, 2003). In fact, using the isotope composition of water vapour entering the stratosphere of  $\delta\text{D}(\text{H}_2\text{O}) = -679\%$  and  $\delta^{18}\text{O}(\text{H}_2\text{O}) = -128\%$  as measured by Johnson et al. (2001), a mean slope  $m = 5.4$  is calculated. Due to the mass-dependent nature of isotope fractionation processes in the troposphere,  $\Delta^{17}\text{O}(\text{H}_2\text{O})$  is set to 0‰ at the tropical tropopause. Potential deviations from this assumption e.g. owing to an interplay of equilibrium and kinetic isotope fractionation factors with different three-isotope relationships (Eq. 1) were not observed yet and thus are not considered.

In this paper, we define mass-independent fraction (MIF) by using the formulation

$$\Delta^{17}\text{O} = [\ln(1 + \delta^{17}\text{O}/1000) - \lambda \cdot \ln(1 + \delta^{18}\text{O}/1000)] \cdot 1000\% \quad (1)$$

suggested by Miller (2002) which quantifies the deviation from mass-dependent fractionation without approximation. As three isotope exponent we adopt  $\lambda = 0.528$  ( $\pm 0.0015$ ) as measured by Meijer and Li (1998) in a large number of natural waters showing  $\delta^{18}\text{O}(\text{H}_2\text{O})$  values between  $-50$  and  $+10\%$ . This value is very close to  $\lambda = 0.529$  derived by Young et al. (2002) for equilibrium fractionation processes, but larger than  $\lambda = 0.513$  inferred for kinetic fractionation processes. It is not known to date, if kinetic fractionation during the upward transport to the tropopause results in significantly lower  $\lambda$  values for H<sub>2</sub>O at the tropopause. Assuming  $\delta^{18}\text{O}(\text{H}_2\text{O}) = -128\%$  at the tropical tropopause and  $\lambda = 0.513$  (which is also the  $\lambda$  value for O<sub>2</sub>), Eq. (1) leads to only 2.05‰ lower  $\delta^{17}\text{O}(\text{H}_2\text{O})$  values. This in an exaggerated upper limit, since  $\lambda$  is certainly not that different for the entire condensation history. In any case, such a shift would not alter much our model results.

In conclusion, it can be presumed that tropospheric water vapour entering the stratosphere at the tropical tropopause on average exhibits a  $\delta\text{D}(\text{H}_2\text{O})/\delta^{18}\text{O}(\text{H}_2\text{O})$  ratio of 5–6 and is mass-dependently fractionated (MDF). Possible local deviations from these two assumptions, e.g. assumed to occur in the outflow of a deep convection cells will be negligible for the H<sub>2</sub>O isotope budget and are not considered here.

In the stratosphere chemical reactions modify this isotope signature imported from the troposphere, as will be pointed out briefly below and explained in more detail later:

(i) The first “chemical” mechanism is the in-situ source of H<sub>2</sub>O, the oxidation of methane (and H<sub>2</sub>). Methane is oxidized in the middle atmosphere by reactions with OH, Cl, and O(<sup>1</sup>D), and by photolysis (Lary and Toumi, 1997). Each oxidized CH<sub>4</sub> molecule leads to the net formation of almost two H<sub>2</sub>O molecules (Evans et al., 1999; Zöger et al., 1999; Michelsen et al., 2000). The  $\delta\text{D}$  value of the produced H<sub>2</sub>O molecule  $\delta\text{D}(\text{H}_2\text{O})$  differs from  $\delta\text{D}(\text{CH}_4)$ , because the CH<sub>4</sub> loss reactions are accompanied by unusually strong kinetic isotope fractionation. For instance, at room temperature the D isotope fractionation factor  $\text{KIE}^{\text{D}}$ , that is the ratio of the

rate constants  $k(\text{CH}_4)/k(\text{CH}_3\text{D})$ , is  $\text{KIE}^{\text{D}}(\text{OH})=1.29$  for the reaction of CH<sub>4</sub> with OH,  $\text{KIE}^{\text{D}}(\text{Cl})=1.51$  for the reaction with Cl, and  $\text{KIE}^{\text{D}}(\text{O}^{1\text{D}})=1.11$  for the reaction with O(<sup>1</sup>D) (Saueressig et al., 1996, 2001; Tyler et al., 2000). Since these KIEs differ considerably, the  $\delta\text{D}(\text{H}_2\text{O})$  distribution in the middle atmosphere is expected to be determined by the partitioning of the different CH<sub>4</sub> oxidation reactions.

(ii) Re-cycling of oxygen atoms between H<sub>2</sub>O and the oxygen reservoir gases O<sub>2</sub> and O<sub>3</sub> via HO<sub>x</sub> and NO<sub>x</sub> species and oxygen isotope exchange reactions. Besides net H<sub>2</sub>O formation due to CH<sub>4</sub> oxidation, continuous loss of H<sub>2</sub>O and reformation of H<sub>2</sub>O lead to an extensive turnover of oxygen atoms between oxygen containing trace gases. This process recycles much more H<sub>2</sub>O molecules than are net produced by the oxidation of CH<sub>4</sub> (see Fig. 5). Though a zero-cycle with respect to the H<sub>2</sub>O mass, it strongly influences the oxygen isotope composition of H<sub>2</sub>O. This process is expected to dominate the MIF oxygen isotope signal from O<sub>3</sub> to H<sub>2</sub>O. Further processes to be considered are a few oxygen isotope exchange reactions such as between OH and H<sub>2</sub>O and NO<sub>2</sub> and H<sub>2</sub>O.

A crucial and exciting point is that more than 99% of all oxygen atoms that end up in H<sub>2</sub>O in the middle atmosphere stem from the hydroxyl radical OH. Hence,  $\delta^{17}\text{O}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  data provide information about the oxygen isotope composition of OH, and by considering  $\Delta^{17}\text{O}(\text{H}_2\text{O})$  about the affection of MIF enriched O<sub>3</sub> upon OH<sub>x</sub> and via OH<sub>x</sub> upon many other oxygen containing trace gases in the middle atmosphere. This MIF transfer from O<sub>3</sub> to oxygen-containing radicals was first studied by Lyons (2001).

## 4 Model description

Our 1-D model encompasses 65 boxes from 15 to 80 km, each 1 km high. Temperature and pressure profiles are set according to the U.S. Standard Atmosphere (1976). Vertical transport is parameterised by eddy diffusion coefficients  $K_z$ , below 29 km using the “National Academy of Science (1976)” profile, from 29 km to 50 km using the “Hunten” profile, both depicted by Massie and Hunten (1981), and above 50 km employing the profile given by Froidevaux and Yung (1982).

### 4.1 Peculiarities in modelling isotope ratios

The concept of chemical families frequently applied in atmospheric chemistry models mostly fails if isotopologues are considered. For instance, the reaction chain of  $\text{CO}+\text{OH}\rightarrow\text{CO}_2+\text{H}$  followed by  $\text{H}+\text{O}_2+\text{M}\rightarrow\text{HO}_2+\text{M}$  converts OH to HO<sub>2</sub>, which conserves the sum of  $\text{HO}_x=\text{OH}+\text{HO}_2$ . The oxygen atom of the initial OH, however, is incorporated in CO<sub>2</sub> and thus leaves the HO<sub>x</sub> family. A new OH bond is formed, which has the oxygen isotope composition of O<sub>2</sub>.

The following peculiarities also have to be taken into account:

- (i) Kinetic isotope fractionation factors that account for the mostly slower reaction rate of the isotopically substituted molecule compared to the most abundant isotopologue.
- (ii) Isotope exchange reactions such as the fast O exchange between O<sub>2</sub> and O(<sup>3</sup>P) (Kaye and Strobel, 1983). They modify isotope ratios but not the concentration of the participating compounds.
- (iii) When including isotopologues and isotopomers that contain two or more atoms of the same element at non-equivalent positions such as O<sub>3</sub> or HO<sub>2</sub>, the individual isotopomers have to be considered separately, e.g. the OQO and OOQ or HQO and HOQ (with Q substituting for <sup>17</sup>O and <sup>18</sup>O).

### 4.2 Trace gas chemistry

Due to negligible cloud formation in the middle atmosphere, our model is restricted to gas phase chemistry. If not cited differently, all reaction rates are taken from JPL (2003). Initially, all reactions involved in H<sub>2</sub>O chemistry and isotope exchange with other gases were assessed carefully for all altitudes covered by the model. The reactions finally used (Tables 1 and 2) always account for more than 95% of the local chemical turnover of H<sub>2</sub>O and its isotopologues at a given altitude.

Water vapour is formed due to H-abstraction by OH, i.e.  $\text{XH}_i+\text{OH}\rightarrow\text{XH}_{i-1}+\text{H}_2\text{O}$ , where XH<sub>i</sub> is CH<sub>4</sub> (Reaction R1), CH<sub>2</sub>O (R8), HO<sub>2</sub> (R16), HCl (R21), H<sub>2</sub> (R26), or HNO<sub>3</sub> (R29). The major sinks of middle atmospheric H<sub>2</sub>O are the reaction with O(<sup>1</sup>D) (R30) and photolysis at wavelength below 200 nm (R31).

Furthermore, all reactions that are necessary to maintain the overall budget of O- and H-atoms balanced are included. To this end a complete methane destruction scheme (LeTexier et al., 1988) and all relevant reactions affecting the HO<sub>x</sub>-family (Burnett and Burnett, 1995) are considered.

The concentrations and the isotopic compositions of H<sub>2</sub>O, OH, HO<sub>2</sub>, H, H<sub>2</sub>, CH<sub>4</sub>, CH<sub>3</sub>, CH<sub>2</sub>O, HCO, HNO<sub>3</sub>, and HCl are explicitly calculated by the model.

### 4.3 Isotope chemistry

Integration of isotopologues renders the model complex, as shown for the initial steps of the major methane destruction reactions (Table 3).

Only for a few of the reactions listed in Table 1 the isotope fractionation factor  $\text{KIE}=k/k'$  is known, with  $k'$  being the rate constant for the isotopically substituted species. All KIEs that have been measured in the laboratory are implemented in the model (Table 5), expressed in the form:

$$\text{KIE} = A \cdot \exp(E/T) \quad (2)$$

**Table 1.** Considered gas phase reactions.

No	reaction	rate <sup>a</sup>		br, n <sup>b</sup>	
		A	E		
(R1)	CH <sub>4</sub> +OH→CH <sub>3</sub> +H <sub>2</sub> O		Table 3		
(R2)	CH <sub>4</sub> +O( <sup>1</sup> D)→...		Table 3		
(R3)	CH <sub>4</sub> +Cl→CH <sub>3</sub> +HCl		Table 3		
(R4)	CH <sub>4</sub> +γ→CH <sub>3</sub> +H		Table 3		
(R5)	CH <sub>3</sub> +O <sub>2</sub> +M→CH <sub>3</sub> O <sub>2</sub> +M		Table 2		
(R6)	CH <sub>3</sub> O <sub>2</sub> +NO→CH <sub>3</sub> O+NO <sub>2</sub>	2.8(-12)		-300	
(R7)	CH <sub>3</sub> O+O <sub>2</sub> →CH <sub>2</sub> O+HO <sub>2</sub>	3.9(-14)		900	
(R8)	CH <sub>2</sub> O+OH→CHO+H <sub>2</sub> O	1.0(-11)		0	
(R9)	CH <sub>2</sub> O+γ→CHO+H/CO+H <sub>2</sub>		altitude dependent		
(R10)	CH <sub>2</sub> O+O( <sup>3</sup> P)→CHO+OH	3.4(-10)		1600	
(R11)	CH <sub>2</sub> O+Cl→CHO+HCl	8.1(-11)		30	
(R12)	HCO+O <sub>2</sub> →CO+HO <sub>2</sub>	3.5(-12)		-140	
(R13)	H+O <sub>2</sub> +M→HO <sub>2</sub> +M		Table 2		
(R14)	H+O <sub>3</sub> →OH+O <sub>2</sub>	1.4(-10)		470	
(R15) <sup>a</sup>	H+HO <sub>2</sub> →2OH	8.1(-11)		0	0.87
(R15) <sup>b</sup>	H+HO <sub>2</sub> →H <sub>2</sub> O+O <sub>2</sub>	8.1(-11)		0	0.09
(R15) <sup>c</sup>	H+HO <sub>2</sub> →H <sub>2</sub> O+O( <sup>3</sup> P)	8.1(-11)		0	0.02
(R16)	OH+HO <sub>2</sub> →H <sub>2</sub> O+O <sub>2</sub>	4.8(-11)		-250	
(R17)	OH+O <sub>3</sub> →HO <sub>2</sub> +O <sub>2</sub>	1.6(-12)		940	
(R18)	OH+O( <sup>3</sup> P)→H+O <sub>2</sub>	2.2(-11)		-120	
(R19)	OH+OH→H <sub>2</sub> O+O( <sup>3</sup> P)	4.2(-12)		240	
(R20)	OH+NO <sub>2</sub> +M→HNO <sub>3</sub> +M		Table 2		
(R21)	HCl+OH→H <sub>2</sub> O+Cl	2.6(-12)		350	
(R22)	CO+OH→CO <sub>2</sub> +H	1.5(-13)		0	
(R23)	HO <sub>2</sub> +NO→OH+NO <sub>2</sub>	3.5(-12)		-250	
(R24)	HO <sub>2</sub> +O( <sup>3</sup> P)→OH+O <sub>2</sub>	3.0(-11)		-200	
(R25)	HO <sub>2</sub> +O <sub>3</sub> →OH+2·O <sub>2</sub>	1.1(-14)		500	
(R26)	H <sub>2</sub> +OH→H <sub>2</sub> O+H	5.5(-12)		2000	
(R27)	H <sub>2</sub> +O( <sup>1</sup> D)→H+OH	1.1(-10)		0	
(R28)	H <sub>2</sub> +Cl→H+HCl	3.7(-11)		2300	
(R29)	HNO <sub>3</sub> +OH→H <sub>2</sub> O+NO <sub>3</sub>				
(R30)	H <sub>2</sub> O+O( <sup>1</sup> D)→2·OH	2.2(-10)		0	
(R31) <sup>a</sup>	H <sub>2</sub> O+γ→H+OH, γ=121.6 nm	5.25(-6)		-4.4(-19)	0.917
(R31) <sup>b</sup>	H <sub>2</sub> O+γ→H+OH, γ>130 nm	1.20(-6)		-1.0(-7)	0.35

<sup>a</sup> rate constant  $k(T)=A \cdot \exp[-(E \cdot K/T)]$  in  $\text{cm}^3 \text{s}^{-1}$

photolysis rate  $j(z)=A \cdot \exp[E \cdot L(z)^n]$  in  $\text{s}^{-1}$ , with  $L(z)$ : number of molecules  $\text{cm}^{-2}$  above altitude  $z$ .

<sup>b</sup> br: branching rate, n: exponent in  $j(z)$

For some KIEs no temperature dependence is known and thus is set constant. For the reactions for which the KIE has not been explicitly measured, KIE is set to  $(\mu'/\mu)^{1/2}$ , with  $\mu=m_1 \cdot m_2/(m_1+m_2)$  being the reduced mass of the reactants of mass  $m_1$  and  $m_2$ . This accounts for the fact that the rate constant of a certain reaction does not only depend on the reactivity of the reactants, but also on their collision frequency and thus thermal speed.

Additionally, the known oxygen exchange reactions were included (Table 5).

#### 4.4 Trace gas parameter profiles

Fixed, globally, seasonally and diurnally averaged profiles are used for the trace gases O<sub>3</sub>, O(<sup>1</sup>D), NO, NO<sub>2</sub>, and Cl. These were derived from a simulation of the Mainz photochemical 2-D model (Groß, 1996), as an annually and diurnally averaged profile of the HNO<sub>3</sub> photolysis frequency.

**Table 2.** Termolecular reactions.

No.	Reaction	$k_0^{300}$ a	n	$k_\infty^{300}$ b	m
(5)	$\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$	$4.5 \times 10^{-31}$	3.0	$1.8 \times 10^{-12}$	1.7
(13)	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	$5.7 \times 10^{-32}$	1.6	$7.5 \times 10^{-11}$	0.0
(20)	$\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	$2.5 \times 10^{-30}$	4.4	$1.6 \times 10^{-11}$	1.7

$$^a k_0(T) = k_0^{300} \cdot \left(\frac{T}{300}\right)^{-n}$$

$$^b k_\infty(T) = k_\infty^{300} \cdot \left(\frac{T}{300}\right)^{-m}$$

$$\text{rate constant } k(M, T) = \left(\frac{k_0(T)[M]}{1 + (k_0(T)[M]/k_\infty(T))}\right) \cdot 0.6^{(1 + [\log_{10}(k_0(T)[M]/k_\infty(T))]^2)^{-1}}$$

[M] being the number concentrations of air molecules and T the temperature.

**Table 3.** Detailed description of the initial methane destruction reactions.

No	reaction	rate		branching ratio	fractionation factor
		A	E		
(1)	$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	2.45 (-12)	1775	1	1
	$\text{CH}_4 + {}^{17}\text{OH} \rightarrow \text{CH}_3 + \text{H}_2 {}^{17}\text{O}$	2.45 (-12)	1775	1	0.986
	$\text{CH}_4 + {}^{18}\text{OH} \rightarrow \text{CH}_3 + \text{H}_2 {}^{18}\text{O}$	2.45 (-12)	1775	1	0.973
	$\text{CH}_4 + \text{OD} \rightarrow \text{CH}_3 + \text{HDO}$	2.45 (-12)	1775	1	Table 4
	$\text{CH}_3\text{D} + \text{OH} \rightarrow \text{CH}_2\text{D} + \text{H}_2\text{O}$	3.5 (-12)	1950	0.75	0.985
	$\text{CH}_3\text{D} + \text{OH} \rightarrow \text{CH}_3 + \text{HDO}$	3.5 (-12)	1950	0.25	0.985
	$\text{CH}_3\text{D} + \text{OD} \rightarrow \text{CH}_2\text{D} + \text{HDO}$	3.5 (-12)	1950	0.75	0.971
	$\text{CH}_3\text{D} + \text{OD} \rightarrow \text{CH}_3 + \text{D}_2\text{O}$	3.5 (-12)	1950	0.25	0.971
(2)	$\text{CH}_4 + \text{O}({}^1\text{D}) \rightarrow \text{CH}_3 + \text{OH}$	1.5 (-10)	0	0.75	1
	$\text{CH}_4 + {}^{17}\text{O}({}^1\text{D}) \rightarrow \text{CH}_3 + {}^{17}\text{OH}$	1.5 (-10)	0	0.75	0.985
	$\text{CH}_4 + {}^{18}\text{O}({}^1\text{D}) \rightarrow \text{CH}_3 + {}^{18}\text{OH}$	1.5 (-10)	0	0.75	0.972
	$\text{CH}_4 + \text{O}({}^1\text{D}) \rightarrow \text{CH}_3\text{O} + \text{H}$	1.5 (-10)	0	0.20	1
	$\text{CH}_4 + {}^{17}\text{O}({}^1\text{D}) \rightarrow \text{CH}_3 {}^{17}\text{O} + \text{H}$	1.5 (-10)	0	0.20	0.985
	$\text{CH}_4 + {}^{18}\text{O}({}^1\text{D}) \rightarrow \text{CH}_3 {}^{18}\text{O} + \text{H}$	1.5 (-10)	0	0.20	0.972
	$\text{CH}_4 + \text{O}({}^1\text{D}) \rightarrow \text{CH}_2\text{O} + \text{H}_2$	1.5 (-10)	0	0.05	1
	$\text{CH}_4 + {}^{17}\text{O}({}^1\text{D}) \rightarrow \text{CH}_2 {}^{17}\text{O} + \text{H}_2$	1.5 (-10)	0	0.05	0.985
	$\text{CH}_4 + {}^{18}\text{O}({}^1\text{D}) \rightarrow \text{CH}_2 {}^{18}\text{O} + \text{H}_2$	1.5 (-10)	0	0.05	0.972
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CH}_3 + \text{OD}$	1.5 (-10)	0	0.75-0.70	Table 4
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CH}_2\text{D} + \text{OH}$	1.5 (-10)	0	0.25-0.70	Table 4
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CH}_2\text{DO} + \text{H}$	1.5 (-10)	0	0.75-0.20	Table 4
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CH}_3\text{O} + \text{D}$	1.5 (-10)	0	0.25-0.20	Table 4
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CHDO} + \text{H}_2$	1.5 (-10)	0	0.75-0.05	Table 4
	$\text{CH}_3\text{D} + \text{O}({}^1\text{D}) \rightarrow \text{CH}_2\text{O} + \text{HD}$	1.5 (-10)	0	0.25-0.05	Table 4
	(3)	$\text{CH}_4 + \text{Cl} \rightarrow \text{CH}_3 + \text{HCl}$	1.1 (-11)	1400	1
$\text{CH}_3\text{D} + \text{Cl} \rightarrow \text{CH}_3 + \text{DCl}$		1.1 (-11)	1400	0.25	Table 4
$\text{CH}_3\text{D} + \text{Cl} \rightarrow \text{CH}_2\text{D} + \text{HCl}$		1.1 (-11)	1400	0.75	Table 4
(4)	$\text{CH}_4 + \gamma \rightarrow \text{CH}_3 + \text{H}$	5.5 (-6)	-4.4(-19)	1	n=0.917 <sup>a</sup>
	$\text{CH}_3\text{D} + \gamma \rightarrow \text{CH}_3 + \text{D}$	5.5 (-6)	-4.4(-19)	0.25	n=0.917 <sup>a</sup>
	$\text{CH}_3\text{D} + \gamma \rightarrow \text{CH}_2\text{D} + \text{H}$	5.5 (-6)	-4.4(-19)	0.75	n=0.917 <sup>a</sup>

<sup>a</sup> Brasseur and Solomon (1986), with photolysis rate  $j(z) = A \cdot \exp[-L(z)^n]$  in  $\text{s}^{-1}$ , L(z) being the number of molecules per  $\text{cm}^2$  above altitude z.

#### 4.5 Isotope parameter profiles of O(<sup>3</sup>P), O<sub>3</sub>, O(<sup>1</sup>D), and NO

The oxygen isotope compositions assumed for O<sub>2</sub>, O(<sup>3</sup>P), O<sub>3</sub>, and O(<sup>1</sup>D) are indicated in Fig. 1 together with the calculated isotope profiles for NO, OH, and HO<sub>2</sub>.

The isotope composition of

(i) O<sub>2</sub> is  $\delta^{17}\text{O}(\text{O}_2) = 11.78\text{‰}$  and  $\delta^{18}\text{O}(\text{O}_2) = 22.96\text{‰}$  (Luz et al., 1999; Coplen et al., 2002),

(ii) O(<sup>3</sup>P) is controlled by the rapid exchange reaction with O<sub>2</sub> (Kaye and Strobel, 1983), which shows significant

**Table 4.** Considered fractionation factors, defined as  $\text{KIE}(T)=\text{KIE}(0) \cdot \exp(B/T)$ .

No	reaction	KIE(0)	B <sup>a</sup>	KIE(300K)	reference
(1)	CH <sub>3</sub> D+OH→CH <sub>2</sub> D+H <sub>2</sub> O	0.605	215.00	1.239	Gierczak et al. (1997)
(1)	CH <sub>4</sub> +OD→CH <sub>3</sub> +HDO	1.120	-55.00	0.932	Gierczak et al. (1997)
(2)	CH <sub>3</sub> D+O( <sup>1</sup> D)→CH <sub>3</sub> +OD	1.060	0.00	1.060	Saueressig et al. (2001)
(3)	CH <sub>3</sub> D+Cl→CH <sub>3</sub> +DCI	1.278	51.31	1.516	Saueressig et al. (1996)
(8)	CHDO+OH→HCO+HDO	0.7812	0.00	0.781	Feilberg et al. (2004)
(8)	CH <sub>2</sub> Q+OH→HCO+H <sub>2</sub> Q	1.0341	0.00	1.034	Feilberg et al. (2004)
(11)	CHDO+Cl→HCO+DCI	0.8326	0.00	0.833	Feilberg et al. (2004)
(11)	CH <sub>2</sub> Q+Cl→HCQ+DCI	0.9259	0.00	0.926	Feilberg et al. (2004)
(26)	HD+OH→HDO+H	1.100	130.00	1.697	JPL (2003)
(27)	HD+O( <sup>1</sup> D)→H+OD	1.130	0.00	1.130	Talukdar and Ravishankara (1996)

<sup>a</sup> if B = 0, no temperature dependency has been measured so far.

**Table 5.** Considered oxygen isotope exchange reactions.

No	reaction	Rate		reference
		A	E	
(32)	QH+NO⇌OH+NQ	1.8(-11)	0	Dubey et al. (1997)
(33)	QH+NO <sub>2</sub> ⇌OH+NOQ	1.0(-11)	0	Greenblatt and Howard (1989)
(34)	QH+H <sub>2</sub> O⇌OH+H <sub>2</sub> Q	1.6(-13)	2100	Greenblatt and Howard (1989)
(35)	HOQ+OH⇌HO <sub>2</sub> +QH	1.7(-11)	-400	Dransfeld and Wagner (1987)
(36)	Q+O <sub>2</sub> ⇌OQ+O			see Sect. 4.5
(37)	Q+NO⇌O+NQ			see Sect. 4.5
(38)	NOQ+H <sub>2</sub> O⇌NO <sub>2</sub> +H <sub>2</sub> Q	2.3(-13)	2100	Jaffe and Klein (1966)
(39)	QH+O <sub>2</sub> ⇌OH+OQ	<1(-17)	0	Greenblatt and Howard (1989)
(40)	HOQ+O <sub>2</sub> ⇌HO <sub>2</sub> +OQ	<3(-17)	0	Sinha et al. (1987)
(41)	NOQ+O <sub>2</sub> ⇌NO <sub>2</sub> +OQ	<1(-24)	0	Sharma et al. (1970)

fractionation and leads to  $\delta^{17}\text{O}(\text{O}(\text{}^3\text{P}))=-27.58\text{‰}$  and  $\delta^{18}\text{O}(\text{O}(\text{}^3\text{P}))=-55.30\text{‰}$  (Johnston et al., 2000).

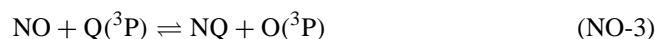
(iii) O<sub>3</sub> was set to be solely dependent on temperature, because all laboratory data indicate negligible pressure dependence below 100 hPa and because it appears that all reliable atmospheric data agree with the enrichments determined in laboratory studies (Johnson et al., 2000; Mauersberger et al., 2001). The (consistent) laboratory data by Thiemens and Jackson (1988, 1990), Morton et al. (1990), and (Günther et al., 1999) are implemented under the assumption that 80% of the isotope enrichment of O<sub>3</sub> is carried by the asymmetric QOO (Anderson et al., 1989; Janssen et al., 1999; Mauersberger et al., 1999).

Q(<sup>1</sup>D) is derived from the isotope enrichment in O<sub>3</sub> under the following further assumptions: (i) during the photolysis of O<sub>3</sub> only the terminal oxygen atoms form O(<sup>1</sup>D), (ii) there is negligible fractionation during the photolysis of O<sub>3</sub> (Wen and Thiemens, 1993), and (iii) mass-dependent collision rates during subsequent quenching of O(<sup>1</sup>D) on N<sub>2</sub> and O<sub>2</sub> to the ground state O(<sup>3</sup>P) lead to additional isotope enrichment of 19‰ for  $\delta^{17}\text{O}$  and 36‰ for  $\delta^{18}\text{O}$  in O(<sup>1</sup>D) (calculated by using the formula given in Sect. 4.3).

The oxygen isotope composition of middle atmospheric NO<sub>x</sub> is not controlled by its main source, i.e. oxidation of N<sub>2</sub>O by O(<sup>1</sup>D), but by O exchange between O<sub>x</sub> and NO<sub>x</sub>:

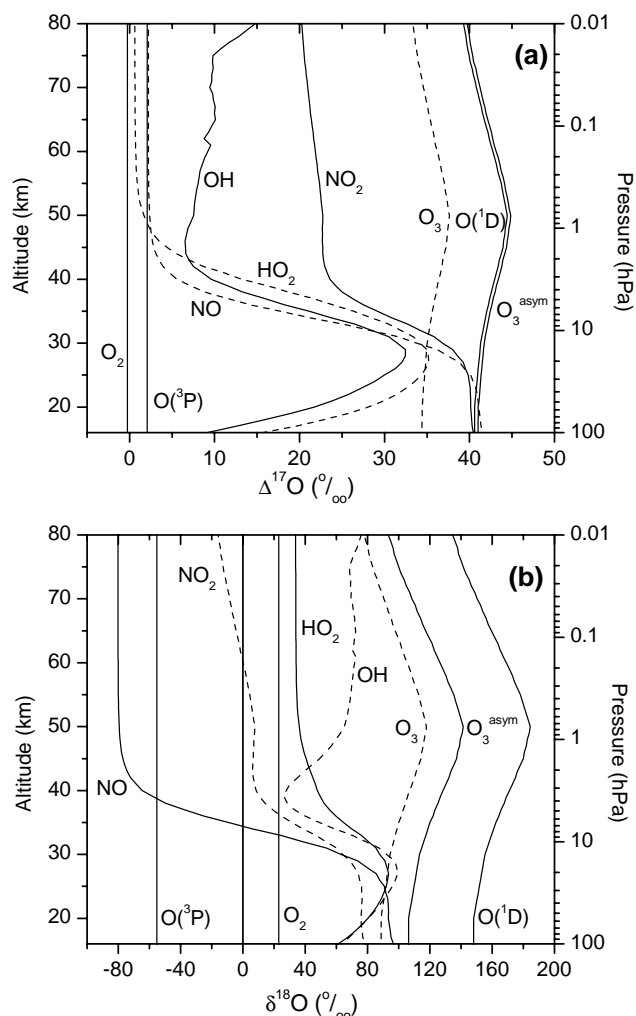


and the fast O-exchange reactions:



Indeed, because of the rapid photochemical cycling less than 0.5% of all O atoms in NO stem from the oxidation of N<sub>2</sub>O by O(<sup>1</sup>D) over the entire altitude range considered. Hence, the isotopic composition of N<sub>2</sub>O that is known to carry a small degree of MIF into the stratosphere (Cliff and Thiemens, 1997; Cliff et al., 1999; Röckmann et al., 2001a; Röckmann et al., 2001b; Kaiser and Röckmann, 2005) does not need to be considered. Using a sub-model, the O isotope ( $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ ) parameter profile of NO is derived by calculating the source partitioning of the reactions NO-1 to NO-4. The inferred enrichments in NO and NO<sub>2</sub> (Fig. 1) in the



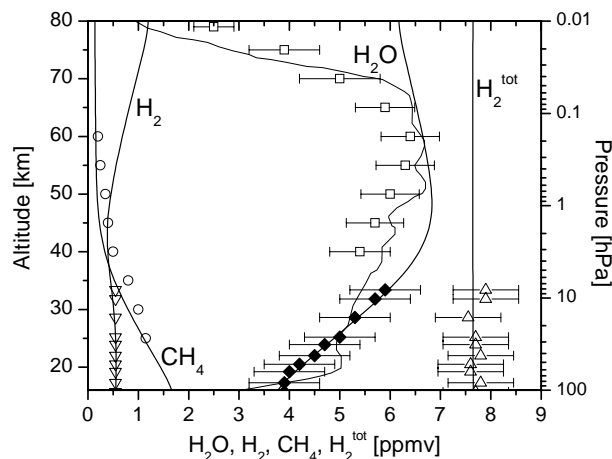


**Fig. 1.** Vertical profile of  $\Delta^{17}\text{O}$  (graph a) and  $\delta^{18}\text{O}$  (graph b) assumed for  $\text{O}_2$ ,  $\text{O}(^3\text{P})$ ,  $\text{O}_3$ , asymmetric  $\text{O}_3$ , and  $\text{O}(^1\text{D})$ , and calculated for  $\text{NO}$ ,  $\text{OH}$  and  $\text{HO}_2$  (without considering the isotope exchange reactions R39 and R40).

lower stratosphere (which is due to the O exchange with  $\text{O}_3$ , reactions NO-1 and NO-2) is only about half the ones calculated by Lyons (2001), explanation in Sect. 7. Because of the dominance of NO-3, the oxygen isotopic composition of NO in the mesosphere is similar to the one of  $\text{O}(^3\text{P})$ .

#### 4.6 Boundary conditions

At the lower model boundary, i.e. the tropopause, fixed trace gas and isotope mixing ratios are set as follows:  $[\text{H}_2\text{O}] = 3.70 \mu\text{mol/mol}$ .  $\delta\text{D}(\text{H}_2\text{O}) = -660\text{‰}$  and  $\delta^{18}\text{O}(\text{H}_2\text{O}) = -128\text{‰}$  (Moyer et al., 1996; Johnson et al., 2001, Kuang et al., 2003, McCarthy et al., 2004).  $\Delta^{17}\text{O}(\text{H}_2\text{O})$  is set to 0‰ (as no process is known in the troposphere, which could cause MIF in  $\text{H}_2\text{O}$ ), so that  $\delta^{17}\text{O}(\text{H}_2\text{O})$  is  $-69.76\text{‰}$  (in agreement with  $-(84 \pm 31)\text{‰}$  observed by Johnson et al., 2001).  $[\text{CH}_4] = 1.70 \mu\text{mol/mol}$ .



**Fig. 2.** Calculated vertical profiles of  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{H}_2$ , and  $\text{H}_2^{\text{tot}}$  compared to measurements of  $\text{H}_2\text{O}$ : balloon-borne in situ Lyman- $\alpha$  hygrometer data at  $43^\circ\text{N}$  (black diamonds) (Zöger et al., 1999), ATMOS data (light squares) (Michelsen et al., 2002), and HALOE data (line) (Nedoluha et al., 1998);  $\text{CH}_4$ ,  $\text{H}_2$ : cryogenic collection and subsequent laboratory analysis at  $43^\circ\text{N}$  (Zöger et al., 1999), and  $\text{H}_2^{\text{tot}}$ : (Zöger et al., 1999).

$\delta\text{D}(\text{CH}_4) = -86\text{‰}$  (Quay et al., 1999).  $[\text{H}_2] = 0.55 \mu\text{mol/mol}$  (Zöger et al., 1999).  $\delta\text{D}(\text{H}_2) = 130\text{‰}$  (Friedman and Scholz, 1974; Rahn et al., 2003; Rhee et al., 2006). The flux of all considered species across the upper boundary (80 km) is set to zero.

## 5 Model results and comparison with observations

The model results presented in this section constitute the “base run” where the badly quantified isotope exchange reactions (R38) to (R41) (Table 5) are omitted. The influence of these badly quantified reactions is assessed in Sect. 6.5.

### 5.1 Vertical trace gas profiles

In Fig. 2 calculated vertical profiles for  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{H}_2$  and the total hydrogen  $\text{H}_2^{\text{tot}}$  are compared with observations. The agreement is good. The difference above 70 km is due to the known strong seasonal variation in this altitude range. For instance,  $\text{H}_2$  is expected to vary between 1 ppmv in July and nearly 3 ppmv in January at 70 km altitude (LeTexier et al., 1988).

The destruction of methane in the stratosphere leads to a relevant increase in water vapour. Maximum mixing ratios of 6.5 ppmv are observed at the stratopause. Above 50 km, increasing loss of  $\text{H}_2\text{O}$  due to reaction with OH and above 65 km due to photolysis overcompensates  $\text{H}_2\text{O}$  formation and causes a decline in  $\text{H}_2\text{O}$  and an increase in  $\text{H}_2$ . The total hydrogen  $\text{H}_2^{\text{tot}}$  stays constant in the middle atmosphere. The weak decrease in the mesosphere comes along with increasing concentrations of atomic hydrogen H.

## 5.2 Vertical profiles of $\delta D(H_2O)$ , $\delta D(CH_4)$ , and $\delta D(H_2)$

The calculated profiles of  $\delta D$  in H<sub>2</sub>O, CH<sub>4</sub>, and H<sub>2</sub> likewise compare well with observations and the model results obtained by Ridal (2002) for  $\delta D(H_2O)$  (Fig. 3).

Apart from the Arctic profile retrieved by (Stowasser et al., 1999), all available  $\delta D(H_2O)$  observations (Sect. 2) (although somewhat differing in absolute concentrations) show a vertical increase by  $\sim(150\text{--}200)\text{‰}$  between 20 and 40 km. This vertical  $\delta D(H_2O)$  increase is due to the increasing fraction of H<sub>2</sub>O that originates from the oxidation of CH<sub>4</sub> (see Sect. 3). The  $\delta D(H_2O)$  value in the mesosphere, which is higher than the tropopause value by  $\sim 250\text{‰}$ , suggests that  $\sim 60\%$  of the mesospheric H<sub>2</sub>O originate from the troposphere and  $\sim 40\%$  stem from the oxidation of CH<sub>4</sub> (see Sect. 6.3).

The  $\delta D$  profiles of CH<sub>4</sub> and H<sub>2</sub> agree well with in-situ sampling and subsequent mass-spectrometric laboratory measurements by Röckmann et al. (2003) and Brass et al. (MPI-K Heidelberg, personal communication).

## 5.3 Vertical Profiles of $\delta^{17}O(H_2O)$ and $\delta^{18}O(H_2O)$

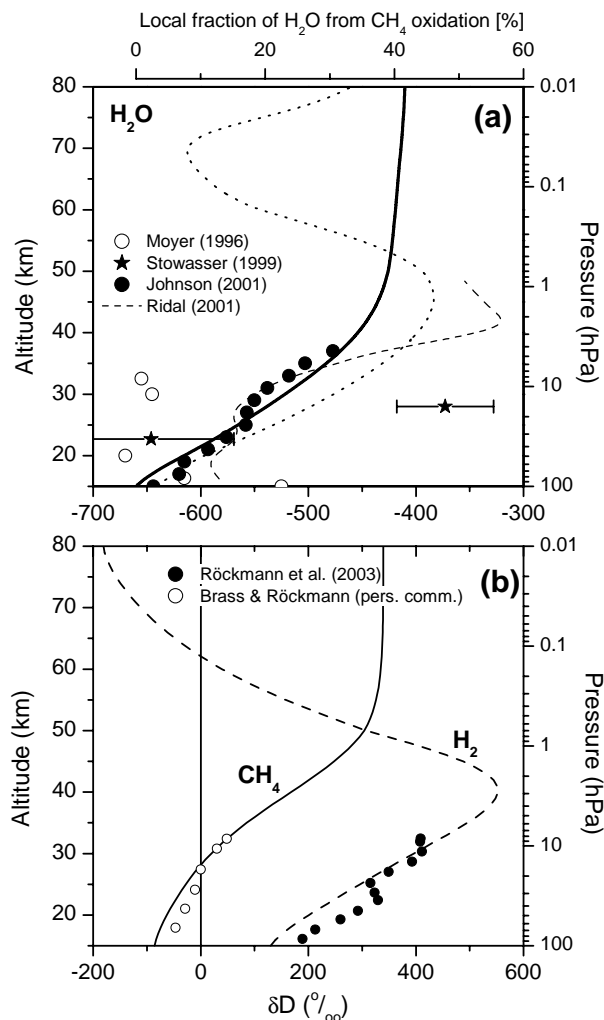
The oxygen isotope ratios in H<sub>2</sub>O (Fig. 4) exhibit a vertical profile that is qualitatively similar to that of  $\delta D(H_2O)$ . However, for the O isotopologues in addition to new H<sub>2</sub>O formation photochemical recycling, that is exchange of oxygen isotopes with O<sub>2</sub> and O<sub>3</sub> via HO<sub>x</sub>- and NO<sub>x</sub>-species, causes additional intensive turnover of  $\delta^{17}O(H_2O)$  and  $\delta^{18}O(H_2O)$ . As a consequence, the relative enrichments are even stronger than for  $\delta D$ , and positive values for  $\delta^{17}O$  and  $\delta^{18}O$  are reached. Note that both recycled H<sub>2</sub>O and newly formed H<sub>2</sub>O have the same O isotope signature since both are produced mainly via HO<sub>x</sub> (see Sect. 6.4).

The measurements by Dinelli et al. (1991), Guo et al. (1989), Rinsland et al. (1991), and Johnson et al. (2001) are in reasonable agreement with our model results. Consider however the large measurement errors of  $\pm(50\text{--}120)\text{‰}$  which is in the same magnitude as the calculated total vertical increase by 85‰ for  $\delta^{17}O(H_2O)$  and 150‰ for  $\delta^{18}O(H_2O)$ .

## 6 Discussion

### 6.1 The budget of middle atmospheric water vapour

Figure 5 exhibits the turnover rates of water vapour in the middle atmosphere. The annual flux of tropospheric water into the stratosphere is set to 788 Mt (Yang and Tung, 1996). In the stratosphere further 63.9 Mt H<sub>2</sub>O (and 0.31 Mt H<sub>2</sub>) is net produced due to the oxidation of CH<sub>4</sub>. The calculated annual CH<sub>4</sub> destruction rate is 30 Mt yr<sup>-1</sup>. This value is slightly lower than the  $(40\pm 10)$  Mt yr<sup>-1</sup> often reported (Crutzen, 1995; Lelieveld et al., 1998), but agrees with Gettelmann et al. (1998) and exceeds earlier values given by Crutzen (1991) and Khalil et al. (1993). The calculated ratios between H<sub>2</sub>O

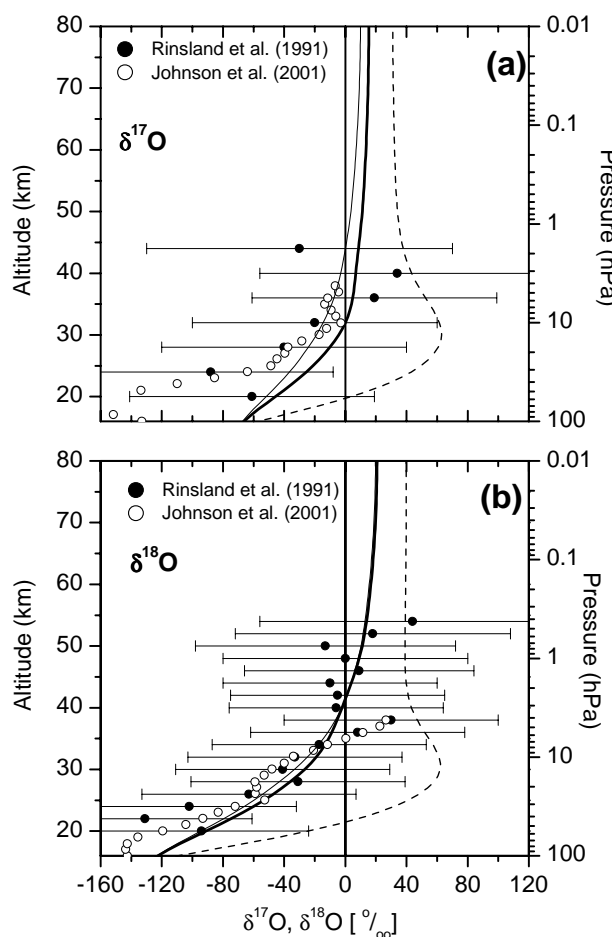


**Fig. 3.** Calculated vertical profile of  $\delta D$  in H<sub>2</sub>O (graph a, thick line), and CH<sub>4</sub> and H<sub>2</sub> (graph b) compared to measurements. **(a)** Dotted line:  $\delta D$  of freshly produced H<sub>2</sub>O. Open circles: ATMOS FTIR data of near-global latitudinal coverage (Moyer et al., 1996). Full circles: Smithsonian Astrophysical Observatory's far-infrared data by Johnson et al. (2001a). Stars: Balloon-borne MIPAS data inside the Arctic vortex at 68° N (Stowasser et al., 1999). Dashed line: 1-D model result by Ridal et al. (2001). Upper x-axis indicates the approximate fraction of H<sub>2</sub>O from the CH<sub>4</sub> oxidation inferred from the  $\delta D(H_2O)$  value (explanation, see Sect. 6.3). **(b)** Full and open circles: Laboratory mass-spectrometer data of in-situ samples.

and H<sub>2</sub> production and CH<sub>4</sub> loss for the entire middle atmosphere are:

$$\frac{P(H_2O)}{L(CH_4)} = 1.90 \quad \text{and} \quad \frac{P(H_2)}{L(CH_4)} = 0.10 \quad (5)$$

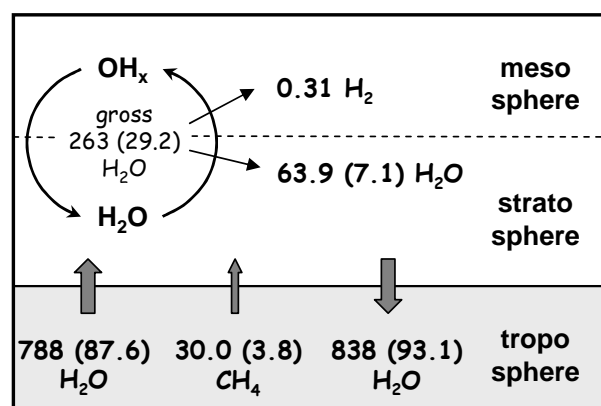
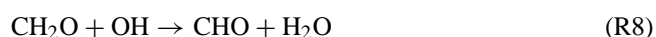
Using a coupled chemistry/dynamical model (LeTexier et al., 1988) derived  $P(H_2O)/L(CH_4)=1.6$  which is in agreement with satellite observations by Hanson and Robinson (1989). More recent in situ measurements indicated higher values of  $1.94\pm 0.27$  (Dessler et al., 1994),  $1.82\pm 0.21$  (Engel et al.,



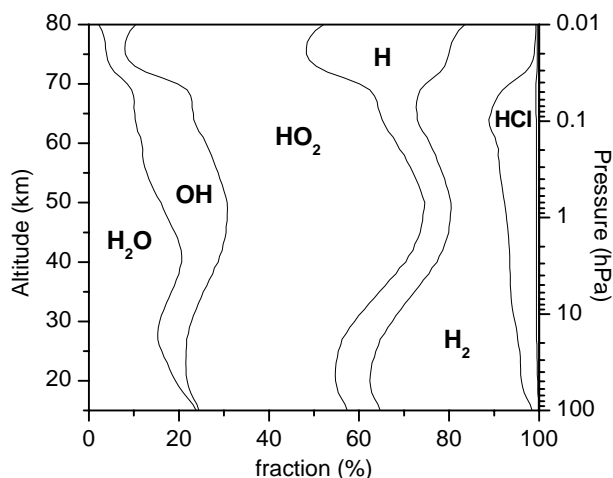
**Fig. 4.** Calculated vertical profiles of  $\delta^{17}\text{O}(\text{H}_2\text{O})$  (graph a) and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  (graph b) compared to ATMOS Spacelab 3 infrared solar spectra near  $30^\circ\text{N}$  (Rinsland et al., 1991) and FTIR balloon-borne data at  $33^\circ$  and  $68^\circ\text{N}$  (Johnson et al., 2001). Thick straight lines: base run. Dashed lines: Oxygen exchange reaction (R38) ( $\text{NOQ} + \text{H}_2\text{O} \rightleftharpoons \text{NO}_2 + \text{H}_2\text{Q}$ ) is considered at its estimated upper limit. Thin straight lines: Oxygen exchange reactions (R39) ( $\text{QH} + \text{O}_2 \rightleftharpoons \text{OH} + \text{OQ}$ ) and (R40) ( $\text{HOQ} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{OQ}$ ) are considered at their estimated upper limits.

1996),  $1.973 \pm 0.003$  (Hurst et al., 1999), and  $1.975 \pm 0.030$  (Zöger et al., 1999), which are in reasonable agreement with our model results.

Interestingly, although each  $\text{CH}_4$  molecule finally results in the formation of almost two  $\text{H}_2\text{O}$  molecules (Eq. 5), most hydrogen atoms in  $\text{CH}_4$  make the detour via other gases to  $\text{H}_2\text{O}$ , as demonstrated in Fig. 6. Only  $\sim 15\%$  of all  $\text{H}_2\text{O}$  molecules are formed directly from one of the four H atoms of  $\text{CH}_4$  or intermediate products in the  $\text{CH}_4$  destruction chain (such as formaldehyde,  $\text{CH}_2\text{O}$ ), i.e., are produced via reactions:



**Fig. 5.** Middle atmospheric budget of  $\text{H}_2\text{O}$ . Numbers are mass fluxes in  $\text{Mt yr}^{-1}$ . Numbers in parenthesis are fluxes of  $\text{H}_2$  in  $\text{Mt yr}^{-1}$ . The  $\text{H}_2\text{O}$  flux into the stratosphere is adopted from Yang and Tung (1996), other numbers are model results.



**Fig. 6.** Calculated percentage fraction of hydrogen atoms that are transferred during the initial oxidation reaction of  $\text{CH}_4$  either to  $\text{H}_2\text{O}$ ,  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{H}$ ,  $\text{H}_2$ , or  $\text{HCl}$ .

The other  $\sim 85\%$  of the H atoms in  $\text{CH}_4$  are incorporated first in  $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{H}_2$ ,  $\text{H}$ , or  $\text{HCl}$ , before ending up in  $\text{H}_2\text{O}$ . This detour the H atoms take from  $\text{CH}_4$  to  $\text{H}_2\text{O}$  certainly affects not only the isotope composition of the final product  $\text{H}_2\text{O}$ , but also that of the intermediate species ( $\text{OH}$ ,  $\text{HO}_2$ ,  $\text{HCO}$ ,  $\text{H}_2$ ,  $\text{H}$ ,  $\text{HCl}$  etc.).

Figure 7 presents the vertical profile of  $\text{H}_2\text{O}$  production  $P(\text{H}_2\text{O})$  and loss  $L(\text{H}_2\text{O})$ . Both  $P(\text{H}_2\text{O})$  (dominated by the reaction  $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$  – Kaye, 1990) and  $L(\text{H}_2\text{O})$  (more than 99% of which are due to the reaction of  $\text{H}_2\text{O} + \text{O}(^1\text{D}) \rightarrow 2\text{OH}$ ) peak at  $\sim 38\text{ km}$  altitude. The net rate,  $P(\text{H}_2\text{O}) - L(\text{H}_2\text{O})$ , amounts to  $\sim 27\%$  of  $P(\text{H}_2\text{O})$  only. It shows a wide maximum centred at  $35\text{--}40\text{ km}$ , that is  $\sim 5\text{ km}$  above the maximum of the  $\text{CH}_4$  loss rate (for better comparison  $2 \times L(\text{CH}_4)$  is shown, dotted line). This again emphasises that during the oxidation of  $\text{CH}_4$  most H atoms are first

incorporated in intermediate species (where the longer lived ones H<sub>2</sub>, HCl, and HNO<sub>3</sub> experience spatial redistribution) before ending up in H<sub>2</sub>O, and that a considerable turnover of H<sub>2</sub>O molecules occurs in the middle atmosphere which significantly exceeds the net production of H<sub>2</sub>O.

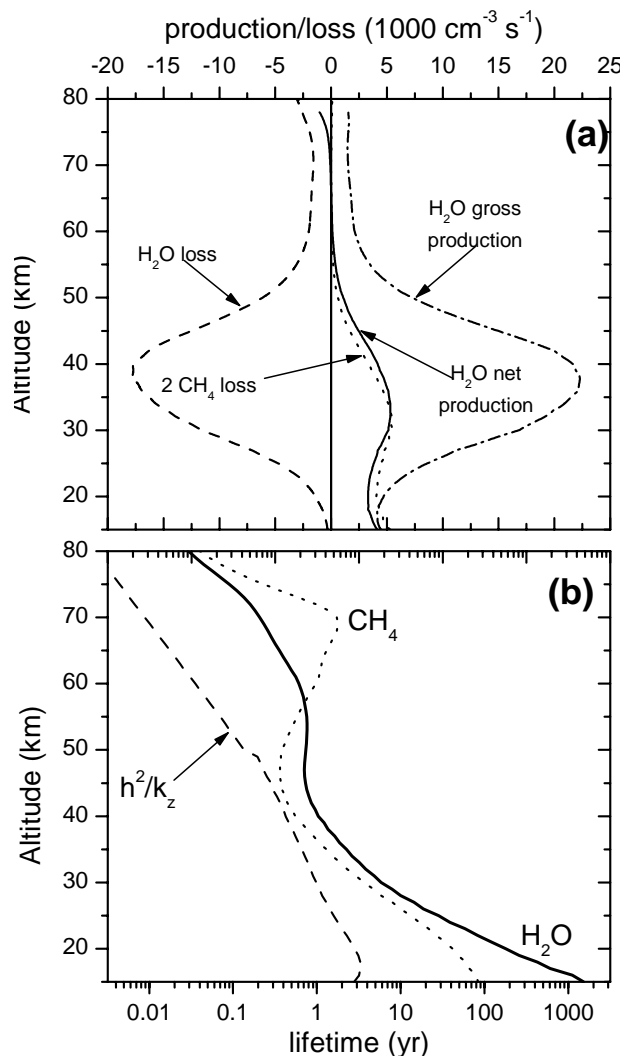
### 6.2 The chemical lifetimes of H<sub>2</sub>O, δD(H<sub>2</sub>O), δ<sup>17</sup>O(H<sub>2</sub>O), and δ<sup>18</sup>O(H<sub>2</sub>O)

Division of the local H<sub>2</sub>O concentration by the local H<sub>2</sub>O loss rate  $L(\text{H}_2\text{O})$  yields the chemical lifetime of H<sub>2</sub>O,  $\tau(\text{H}_2\text{O})$ , at a certain altitude (Fig. 7b). As the same reactions control the loss of HDO molecules, the chemical lifetime of HDO,  $\tau(\text{HDO})$ , is identical with  $\tau(\text{H}_2\text{O})$ . In the entire middle atmosphere  $\tau(\text{H}_2\text{O})$  or  $\tau(\text{HDO})$ , respectively, (like  $\tau(\text{CH}_4)$ ) exceeds the vertical transport time scale  $H^2/K_z$  ( $H$  being the local scale height and  $K_z$  the vertical eddy diffusion coefficient). That is, neither H<sub>2</sub>O nor HDO is in photochemical equilibrium in the middle atmosphere. Only between 35 and 50 km altitude, the transport time scale almost compares with the photochemical lifetime of H<sub>2</sub>O (and HDO), in agreement with (LeTexier et al., 1988). Below 35 km,  $\tau(\text{H}_2\text{O})$  and  $\tau(\text{HDO})$  exceeds ~5 years.

Consider moreover, that the influence of in-situ H<sub>2</sub>O production due to CH<sub>4</sub> oxidation on δD(H<sub>2</sub>O) is small below ~30 km, too. This can be seen in Fig. 7a, when the net H<sub>2</sub>O production (black line) displayed in molecules cm<sup>-3</sup> s<sup>-1</sup> is divided by the pressure, which gives the H<sub>2</sub>O production in ppmv s<sup>-1</sup>. This number peaks at 45 km and is small below ~30 km.

The latter conclusion and the long chemical lifetime implies that below 30–35 km the H<sub>2</sub>O mixing ratio as well as its δD value is largely dominated by transport, i.e. by vertical transport for the present 1-D model. Thus, between the tropopause and 30–35 km the H<sub>2</sub>O mixing ratio and its δD value is determined by (vertical) mixing of two reservoirs, the one at the tropopause which is controlled by (physical) fractionation processes in the troposphere, and the second above 30–35 km which is determined by the dominant H<sub>2</sub>O loss reaction (R30).

For the oxygen isotopologues δ<sup>17</sup>O(H<sub>2</sub>O) and δ<sup>18</sup>O(H<sub>2</sub>O), additional oxygen exchange of H<sub>2</sub>O with other gases (Reactions R34 and R38) causes somewhat shorter lifetimes of the δ<sup>17</sup>O and δ<sup>18</sup>O signature of the stratospheric water vapour. Moreover, the vital recycling of water (via HO<sub>x</sub> species) only weakly affects the δD(H<sub>2</sub>O) value, because H<sub>2</sub>O is the major hydrogen reservoir in the mesosphere. This is not the case for δ<sup>17</sup>O(H<sub>2</sub>O) and δ<sup>18</sup>O(H<sub>2</sub>O), where the many intermediate species involved in the H<sub>2</sub>O recycling process exchange oxygen atoms with the other major oxygen “reservoirs” O<sub>2</sub> and O<sub>3</sub>.



**Fig. 7.** (a) calculated vertical profiles of H<sub>2</sub>O production and loss rates in the middle atmosphere. For comparison, the double CH<sub>4</sub> loss rate is shown (as almost two H<sub>2</sub>O molecules are net produced for each oxidised CH<sub>4</sub> molecule, see Eq. 5). (b) comparison of the photochemical lifetime of H<sub>2</sub>O and CH<sub>4</sub> with the transport time scale ( $h^2/k_z$ , with  $h$ : atmospheric scale height and  $k_z$ : vertical eddy diffusion coefficient).

### 6.3 δD(H<sub>2</sub>O) as tracer for CH<sub>4</sub> oxidation

Tropospheric H<sub>2</sub>O is imported into the stratosphere with δD(H<sub>2</sub>O) ≈ -660‰ (Moyer et al., 1996; Johnson et al., 2001; Kuang et al., 2003; McCarthy et al., 2004). Tropospheric CH<sub>4</sub> carries much higher δD values of roughly -86‰ (Quay et al., 1999) into the stratosphere. The vertically increasing contribution of H<sub>2</sub>O produced by the oxidation of CH<sub>4</sub> is described by the upper x-axis of Fig. 3. It shows the local fraction of H<sub>2</sub>O from CH<sub>4</sub> oxidation  $\mathcal{F}$ , that is the ratio between the difference of the local δD(H<sub>2</sub>O) value to the tropopause value (-660‰) and the difference of the δD(H<sub>2</sub>O) from the

CH<sub>4</sub> oxidation (set to −86‰) and the δD(H<sub>2</sub>O) tropopause value, i.e.,

$$\mathcal{F} = \frac{\delta\text{D}(\text{H}_2\text{O}) - (-660\text{‰})}{-86\text{‰} - (-660\text{‰})} \quad (6)$$

Figure 3 indicates that ~40% of the water vapour present above 40 km originate from the oxidation of CH<sub>4</sub>. For simplicity, we have set δD(CH<sub>4</sub>) constant, although in reality it varies with altitude (Fig. 3b). The influence of this simplification is surprisingly weak. This has two reasons. First, the contributions of the three main CH<sub>4</sub> loss reactions (R1–R3) are comparable throughout the middle and upper stratosphere (where the major CH<sub>4</sub> loss occurs). Second, due to the long chemical lifetime of H<sub>2</sub>O (and HDO), spatial redistribution smears out the anyway weak vertically changing δD(H<sub>2</sub>O) source signature.

Unfortunately, this fact also documents that the δD(H<sub>2</sub>O) value does not constitute a sensitive measure for quantifying the partitioning of the different CH<sub>4</sub> loss reaction chains, contrary to its initial assumption.

Another surprising feature is that both, the δD value of the source molecule CH<sub>4</sub> and the one of the end product H<sub>2</sub>O increase with altitude (Fig. 3), although mass conservation for δD at a first glance suggests the opposite behaviour. In all methane oxidation reactions the most abundant CH<sub>4</sub> reacts faster than the isotopically substituted CH<sub>3</sub>D (Sect. 3). Hence, the remaining CH<sub>4</sub> is continuously enriched in D/H with altitude. The D/H ratio of the freshly formed H<sub>2</sub>O is certainly much lower (dotted line) but is still higher than the D/H ratio of the H<sub>2</sub>O lofted from below. Thus, both the δD value of CH<sub>4</sub> and of freshly produced H<sub>2</sub>O increases with altitude. Note that for an isotope mass balance the δ values must be multiplied with the concentrations. Here, the concentration of the “D-richer” source CH<sub>4</sub> decreases and the concentration of the D-depleted product H<sub>2</sub>O increases. Thus, mass balance is achieved although both δ values increase.

#### 6.4 δ<sup>17</sup>O(H<sub>2</sub>O) and δ<sup>18</sup>O(H<sub>2</sub>O) as tracer for transport and chemistry

As outlined in Sect. 3, the oxygen isotope signature of middle atmospheric water vapour is determined by the partitioning of four oxygen isotope sources: (1) mass-dependently fractionated (MDF) H<sub>2</sub>O imported from the troposphere, (2) mass-independently fractionated (MIF) H<sub>2</sub>O formed as a final product of the oxidation of CH<sub>4</sub>, (3) MIF carrying H<sub>2</sub>O from the recycling of H<sub>2</sub>O via the HO<sub>x</sub> family and (4) oxygen atom exchange between H<sub>2</sub>O and other gases.

The δ<sup>17</sup>O and δ<sup>18</sup>O values of source (1), i.e. of H<sub>2</sub>O imported from the troposphere, are about −67‰ and −128‰, respectively (see Sect. 4.6). The δO values of water produced by the isotope sources (2) to (4) are controlled by the respective educt molecules and the kinetic isotope fractionation factor KIE of the relevant reaction. As outlined by Kaye (1990) and confirmed by our calculations, more than 99% of

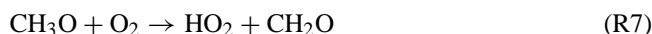
all H<sub>2</sub>O molecules generated in the middle atmosphere are due to hydrogen abstraction reactions by OH. Thus, the isotope sources (2) and (3) will show the O isotope signature of OH at the respective altitude. H<sub>2</sub>O itself undergoes oxygen isotope exchange (i.e. isotope source 4) with OH (R34) and NO<sub>2</sub> (R41, Table 5). Reaction (R34) is too slow to significantly affect the isotope composition of H<sub>2</sub>O. The rate constant of Reaction (R38) was not quantified yet; its potentially considerable impact is addressed in Sect. 6.5.

In conclusion, the modification of the oxygen isotope composition of middle atmospheric H<sub>2</sub>O is controlled by the oxygen isotope composition of OH. For this reason, the oxygen isotope signature of the different OH sources is studied next. Reaction chains where OH is converted into HO<sub>2</sub> and back into OH without breaking the initial OH bond constitute a zero cycle with respect to the oxygen isotopic composition. Thus, only reactions forming new OH bonds need to be considered.

##### 6.4.1 The formation of new OH bonds

The influence of the most important reactions forming new OH bonds are displayed in Fig. 8a. Four classes of reactions, distinguished by the O isotope signal transferred, form new OH<sub>x</sub> bonds:

(i) HO<sub>x</sub> that receives the oxygen isotope signature from molecular oxygen via



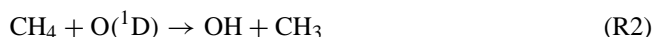
Reactions (R7) and (R12) are part of the CH<sub>4</sub> oxidation chain and only play a role below 40 km. Reaction (R13) clearly dominates the formation of new OH bonds in the mesosphere. In addition, oxygen isotope exchange between HO<sub>x</sub> and O<sub>2</sub> may occur (Reactions R39 and R40) the influence of which are discussed in Sect. 6.5.

(ii) HO<sub>x</sub> that receives the oxygen isotope signature from MIF carrying ozone via



which is important above 40 km only. Although O<sub>3</sub> also influences the isotope composition of HO<sub>2</sub> via OH+O<sub>3</sub>→HO<sub>2</sub>+O<sub>2</sub>, new OH bonds are not formed. The reason is that the oxygen atom that OH receives from O<sub>3</sub> is lost again, simply because HO<sub>2</sub> is an asymmetric molecule (H–O–O).

(iii) HO<sub>x</sub> that receives the oxygen signature from MIF carrying O(<sup>1</sup>D) and, in the case of Reaction (R30), from H<sub>2</sub>O:



**Table 6.** Percentage origin of oxygen isotopes of freshly produced H<sub>2</sub>O averaged over stratosphere and mesosphere.

Oxygen Isotope Source		base run		considering R39–R41		considering R38	
Species	isotope signature	stratosph.	mesosph.	stratosph.	mesosph.	stratosph.	mesosph.
O <sub>2</sub>	MDF <sup>a</sup>	79.5	74.6	98.1	77.5	70.0	74.6
O <sub>3</sub>	MIF <sup>b</sup>	16.5	25.3	1.5	22.4	26.6	25.3
O( <sup>1</sup> D)	MIF <sup>b</sup>	2.1	0.0	0.2	0.0	1.8	0.0
others		1.9	0.1	0.2	0.1	1.6	0.1

<sup>a</sup> MDF = mass-dependently fractionated

<sup>b</sup> MIF = mass-independently fractionated



while the most important of them, Reaction (R30), plays only a modest role between 30 and 45 km.

(iv) HO<sub>x</sub> that receives the oxygen isotope signature from NO<sub>x</sub>:

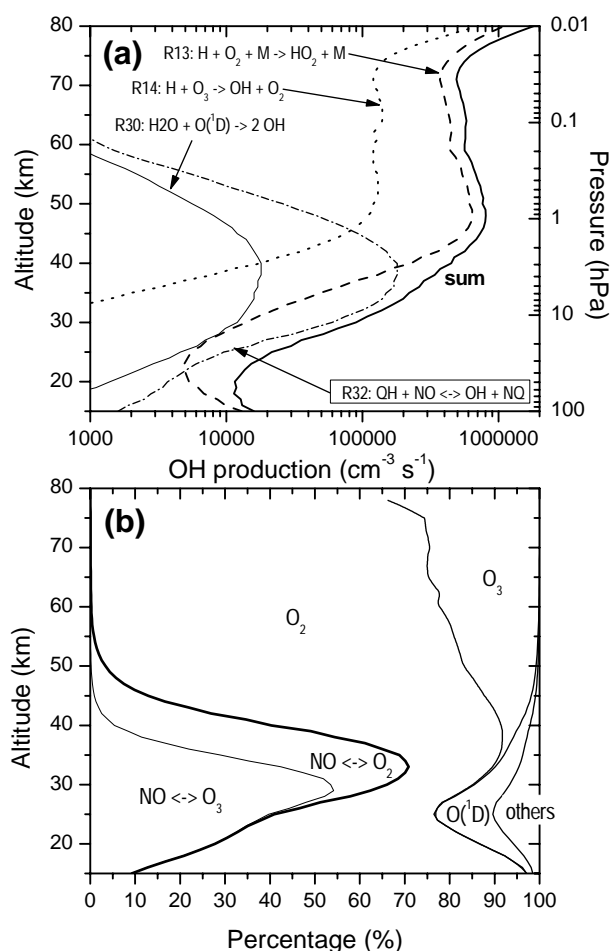


while the oxygen isotope composition of NO<sub>x</sub> is controlled by reactions with the O<sub>2</sub> and O<sub>3</sub> reservoirs (Sect. 4.4).

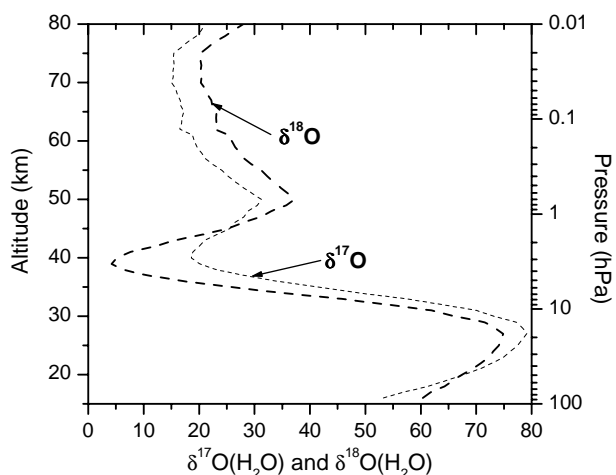
#### 6.4.2 The origin of oxygen atoms incorporated in H<sub>2</sub>O

On the basis of Sect. 6.4.1, the influence of each oxygen source (O<sub>2</sub>, O<sub>3</sub>, O(<sup>1</sup>D)), and NO<sub>x</sub>) for the oxygen isotope composition of freshly produced H<sub>2</sub>O is assessed. As demonstrated in Fig. 8 and listed in Table 6, molecular oxygen clearly dominates as source of oxygen atoms transferred to water vapour in the entire middle atmosphere. In the model base run (R38 to R41 are omitted), of all oxygen isotopes incorporated in H<sub>2</sub>O in stratosphere and mesosphere, respectively, ~78% and ~70% stem from O<sub>2</sub>, ~17% and ~30% from O<sub>3</sub>, ~2% and ~0% from O(<sup>1</sup>D)), and ~2% and ~0% from other gases such as HNO<sub>3</sub> or H<sub>2</sub>O itself (Fig. 8). Another interesting feature is that in the stratosphere ~50% of the overall oxygen isotope transfer to H<sub>2</sub>O proceeds in two steps, that is from O<sub>2</sub> and O<sub>3</sub> to NO<sub>x</sub> and then from NO<sub>x</sub> via HO<sub>x</sub> to H<sub>2</sub>O.

This oxygen isotope source partitioning (Fig. 8, Table 6) is reflected in the strongly structured vertical profiles of δ<sup>17</sup>O(H<sub>2</sub>O) and δ<sup>18</sup>O(H<sub>2</sub>O) of freshly produced H<sub>2</sub>O (Fig. 9). Two maxima occur, both due to oxygen atom transfer from O<sub>3</sub> to H<sub>2</sub>O. In the stratosphere, it is the oxygen transfer chain O<sub>3</sub>  $\xrightarrow{\text{O}}$  NO<sub>x</sub>  $\xrightarrow{\text{O}}$  HO<sub>x</sub>  $\xrightarrow{\text{O}}$  H<sub>2</sub>O. In the mesosphere with the high concentrations of atomic hydrogen, it is caused by H+O<sub>3</sub>→OH+O<sub>2</sub> (Reaction R14) and subsequent O transfer from OH to H<sub>2</sub>O.



**Fig. 8.** (a) Four most important reactions that lead to the formation of new OH bonds. (b) Percentage fraction of oxygen atoms originating from the “reservoirs” O<sub>2</sub>, O<sub>3</sub>, and O(<sup>1</sup>D)) in freshly produced H<sub>2</sub>O. Thick straight lines separate the three different reservoirs. In the stratosphere, considerable oxygen transfer from O<sub>2</sub> and O<sub>3</sub> to H<sub>2</sub>O occurs via the NO<sub>x</sub> family (grey areas).



**Fig. 9.** Vertical profiles of  $\delta^{17}\text{O}(\text{H}_2\text{O})$  and  $\delta^{18}\text{O}(\text{H}_2\text{O})$  of freshly produced H<sub>2</sub>O.

#### 6.4.3 $\Delta^{17}\text{O}(\text{H}_2\text{O})$ as a tracer of MIF transfer from O<sub>3</sub> to H<sub>2</sub>O

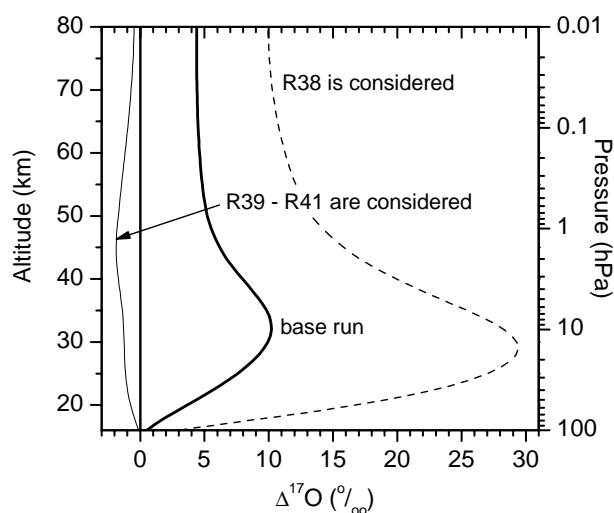
The last Sect. 6.4.2 revealed that the pathway of MIF from O<sub>3</sub> to H<sub>2</sub>O is different compared to the one from O<sub>3</sub> to CO<sub>2</sub>. CO<sub>2</sub> is assumed to receive the MIF signal exclusively from O(<sup>1</sup>D) (produced by the photolysis of O<sub>3</sub>) via the short-lived intermediate CO<sub>3</sub> (Yung et al., 1991, 1997; Barth and Zahn, 1997). In the case of H<sub>2</sub>O, O(<sup>1</sup>D) is only weakly involved in the oxygen isotope transfer (Table 6). In the stratosphere water vapour receives only ~15% of its MIF signal from O(<sup>1</sup>D). In the mesosphere O(<sup>1</sup>D) does not play any role at all.

As indicated in Fig. 8, in the stratosphere MIF transfer from O<sub>3</sub> to H<sub>2</sub>O basically proceeds in three steps, first MIF transfer from O<sub>3</sub> to NO<sub>x</sub> species (via reaction NO-1: NO+O<sub>3</sub>→NO<sub>2</sub>+O<sub>2</sub>, Sect. 4.5), then from NO<sub>x</sub> to OH<sub>x</sub> and finally transfer to H<sub>2</sub>O due to H-abstraction by OH. This quite efficient oxygen transfer chain leads to peaking  $\Delta^{17}\text{O}(\text{H}_2\text{O})$  values of ~10‰ around ~32 km altitude (Fig. 10). In the mesosphere, NO<sub>x</sub> species are not involved. There, the entire MIF transfer from O<sub>3</sub> to HO<sub>x</sub> (and from there to H<sub>2</sub>O) proceeds via Reaction (R14): H+O<sub>3</sub>→OH+O<sub>2</sub>.

#### 6.5 Sensitivity study: Influence of additional oxygen isotope exchange reactions

The results discussed so far constitutes the “base run” in which the already quantified (oxygen) isotope exchange reactions (R32) to (R37) (Table 5) were considered. The last Sect. 6.4 actually revealed the importance of the oxygen isotope exchange reaction (R32) (see Fig. 8) for the oxygen isotope composition of OH and thus freshly produced H<sub>2</sub>O.

If the three further, still unquantified exchange reactions with the O<sub>2</sub> reservoir (R39) to (R41) are considered at their estimated upper limit (Table 5),  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  of water



**Fig. 10.** Calculated vertical profile of  $\Delta^{17}\text{O}(\text{H}_2\text{O})$ . Thick straight line: base run. Dashed line: Oxygen exchange reaction (R38) ( $\text{NOQ}+\text{H}_2\text{O}\rightleftharpoons\text{NO}_2+\text{H}_2\text{Q}$ ) is considered at its estimated upper limit. Thin straight line: Oxygen exchange reactions (R39) ( $\text{QH}+\text{O}_2\rightleftharpoons\text{OH}+\text{OQ}$ ) and (R40) ( $\text{HOQ}+\text{O}_2\rightleftharpoons\text{HO}_2+\text{OQ}$ ) are considered at their estimated upper limits.

vapour (and OH) are slightly lower (thin lines in Fig. 4), but the MIF signal is completely washed out (Fig. 10).

On the contrary, if the isotope exchange reaction (R38) ( $\text{NOQ}+\text{H}_2\text{O}\rightleftharpoons\text{NO}_2+\text{H}_2\text{Q}$ ) is considered at the rate measured forty years ago by Jaffe and Klein (1966), the enrichment in  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  (Fig. 4) as well as the MIF signal (Fig. 10) strongly increases in the stratosphere and reaches values of  $\Delta^{17}\text{O}(\text{H}_2\text{O})\approx 30\text{‰}$  at ~29 km altitude.

This strong sensitivity to isotope exchange reactions documents the urgent need for better quantified rate constants of the relevant reactions.

## 7 Conclusions

Application of a simple 1-D isotope chemistry box model demonstrates that a significant number of chemical reactions with diverse gases cause considerable fractionation of all three stable isotope ratios D/H, <sup>17</sup>O/<sup>16</sup>O, and <sup>18</sup>O/<sup>16</sup>O in middle atmospheric water vapour relative to values at the tropopause. This makes a description much more complicated compared to other trace gases such as CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O.

$\delta\text{D}(\text{H}_2\text{O})$  was modelled to increase from -660‰ at the tropopause to -410‰ above 40 km, which is in excellent agreement with the observations. This increase by ~250‰ corresponds to a fraction of ~40% of H<sub>2</sub>O produced as end product of the oxidation of CH<sub>4</sub>. Although the D fractionation factors of the individual CH<sub>4</sub> oxidation reactions with OH, O(<sup>1</sup>D), and Cl differ strongly, the  $\delta\text{D}(\text{H}_2\text{O})$  value turned out to be no sensitive tracer to distinguish between

the different CH<sub>4</sub> oxidation chains. This has two reasons. First, the major CH<sub>4</sub> loss occurs in the middle and upper stratosphere where the reactions with O(<sup>1</sup>D) which comes along with weak isotope fractionation dominates. Second, the chemical lifetime of H<sub>2</sub>O is long in the middle atmosphere. This allows for significant redistribution and thus weakening of spatial gradients of δD(H<sub>2</sub>O).

The results for the oxygen isotope ratios <sup>17</sup>O/<sup>16</sup>O, and <sup>18</sup>O/<sup>16</sup>O are less robust, because of the many reactions involved in the oxygen isotope transfer from the reservoirs to H<sub>2</sub>O and the many badly or not quantified isotope fractionation factors and oxygen isotope exchange reactions. In the base run, where the Reactions (R38), (R39) and (R40) are not considered, δ<sup>17</sup>O(H<sub>2</sub>O) and δ<sup>18</sup>O(H<sub>2</sub>O) are calculated to increase relative to the tropopause by up to ~85% and ~145%, respectively, which is also in agreement with the observations. Fractionation of the oxygen isotope ratios in H<sub>2</sub>O was demonstrated to be determined almost exclusively by the isotope signature of OH. The oxygen isotopic composition of OH, in turn, is mainly controlled by the one of O<sub>2</sub> that is mass-dependently fractionated (MDF). In the stratosphere and mesosphere, respectively, ~78 and ~70% of all oxygen atoms transferred to H<sub>2</sub>O stem from O<sub>2</sub>, while ~17 and ~30% originate from O<sub>3</sub> that is mass-independently fractionated (MIF). As a result, the calculated MIF signal of H<sub>2</sub>O is only modest and reaches values of Δ<sup>17</sup>O(H<sub>2</sub>O)=10‰ at 30–35 km altitude.

However, if beyond the base run, further badly quantified oxygen isotope exchange reactions with O<sub>2</sub> (R39 and R40) are considered at their estimated upper limit, the MIF signature completely vanishes in middle atmospheric H<sub>2</sub>O. In contrast, if the isotope exchange reaction of H<sub>2</sub>O with NO<sub>2</sub> (Reaction R38) is considered, the MIF signal reaches high values of Δ<sup>17</sup>O(H<sub>2</sub>O)=30‰ around 29 km. Indeed and in any case, the transfer of the MIF signature in O<sub>3</sub> to OH and H<sub>2</sub>O proceeds primarily via NO<sub>x</sub> species in the stratosphere and directly via the reaction of H+O<sub>3</sub>→OH+O<sub>2</sub> in the mesosphere. That is, the MIF transfer from O<sub>3</sub> to H<sub>2</sub>O is quite different from the one from O<sub>3</sub> to CO<sub>2</sub> where it proceeds via O(<sup>1</sup>D) and the intermediate complex CO<sub>3</sub><sup>\*</sup>.

The largest unknowns in our calculations are the unquantified reaction rates of a few oxygen isotope exchange reactions, in particular of OH<sub>x</sub> and NO<sub>x</sub> with O<sub>2</sub>, and the many unquantified isotope fractionation factors of the reactions involved in the isotope transfer to H<sub>2</sub>O. In this respect, the most urgent need in this research field is the development of more precise techniques to measure the isotope composition of water vapour both in the laboratory and atmosphere.

Finally, the calculated MIF signal transferred to HO<sub>x</sub> and thus to H<sub>2</sub>O is only half as large as the one determined by Lyons (2001). This discrepancy arises from the different Δ<sup>17</sup>O signatures assumed for the asymmetric O<sub>3</sub> molecule and O(<sup>1</sup>D). Lyons (2001) used (i) the branching ratios of 0.43 and 0.57 for δ<sup>18</sup>O in the reaction of O+QO→OQO and QOO as measured by Janssen

et al. (1999) for δ<sup>17</sup>O, too, and (ii) the isotope fractionation factors for this reaction measured by Mauersberger et al. (1999). This assumption led to Δ<sup>17</sup>O values of asymmetric O<sub>3</sub> of Δ<sup>17</sup>O(QOO)~85‰, and together with the mean Δ<sup>17</sup>O values of O<sub>3</sub> of Δ<sup>17</sup>O(O<sub>3</sub>)~38‰, to Δ<sup>17</sup>O values of symmetric O<sub>3</sub> of Δ<sup>17</sup>O(OQO)=-50‰ only (because Δ<sup>17</sup>O(O<sub>3</sub>)=2/3 Δ<sup>17</sup>O(QOO)+1/3 Δ<sup>17</sup>O(OQO)). Such a strong difference in Δ<sup>17</sup>O between asymmetric and symmetric ozone is unlikely (C. Janssen, personal communication). In contrast, we assumed identical ratios of the enrichments of δ<sup>17</sup>O and δ<sup>18</sup>O in QOO and OQO. That is, in the stratosphere we apply mean Δ<sup>17</sup>O values of 34‰ for O<sub>3</sub>, which is in agreement with Lyons (2001), but Δ<sup>17</sup>O values of 39‰ for QOO and 25‰ for OQO.

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