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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 ~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 ~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 ~25% for D/H, ~8.5% for  $^{17}\text{O}/^{16}\text{O}$ , and ~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.

▣ [Final Revised Paper](#) (PDF, 357 KB) ▣ [Discussion Paper](#) (ACPD)

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