



Measurement of $\delta^{18}O$ and $\Delta^{17}O$ of water vapor in the UT/LS region

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Exact knowledge about the isotopic composition of water vapor in the tropopause region and the stratosphere provides important information for the understanding of atmospheric transport and photochemistry. For the measurement of the stable isotopologues $H_2^{17}O$ and $H_2^{18}O$ and $H_2^{16}O$, a complete analytical procedure has been developed for the purpose of precise measurements of the mentioned water isotopologues. It consists of three instruments: a continuous-flow system for the chemical decomposition of H_2O to O_2 for subsequent mass-spectrometrical analysis, a calibration unit for the production of water vapor with known isotopic composition, and a cryogenic sampling unit for operation aboard airplanes and balloons. The required sample amount could be reduced to about 100 ng. With these apparatus, samples of atmospheric water vapor have been taken on 4 flights between New Zealand and Antarctica, and have later been analyzed in the laboratory. The results show a strong enhancement in $\delta^{18}O$ with decreasing water vapor mixing ratio in the UT/LS region, which can not be explained by mixing alone. Rather, photochemistry has to be taken into account, which is demonstrated by a 1-D model combining the complete photochemistry of water vapor. The oxygen anomaly $\Delta^{17}O$ is smaller than two permil, putting important constraints on the isotope exchange rate $NO_2 + H_2Q \longleftrightarrow NOQ + H_2O$.