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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heavy hydrogen in the stratosphere" *by* T. Roeckmann et al.

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We thank the referees for the positive reviews. In response to the positive general comments, we point out that the credit for the initial discovery of the strong deuterium enrichment in stratospheric H2 should go to Thom Rahn and colleagues, who first detected this in samples from the NASA ER-2 aircraft. Their paper has now been published (Rahn et al., 2003) during the discussion period of our manuscript and has been incorporated in the revised version of our paper.

Regarding the referees' specific comments:

Referee 1:

We mention the short-lived species in the revised manuscript.

It is highly unlikely that stratospheric ice particles can fall down to the surface. Ice crystals usually evaporate or sublimate again as soon as they leave the region of temperatures below the ice frost point.

Since the branching ratios are dependent on temperature, pressure, and photolysis wavelength which vary strongly throughout the stratosphere, as the referee notes, we prefer not to give exact branching rations.

We have included the suggested reference to figure 1. We are not aware of any studies on the impact on ozone changes on H2 levels in the stratosphere, and therefore prefer not to include speculations on this topic in our paper.

We have changed this section to "... has contributed to, but can not entirely explain the observed increase in stratospheric water vapour."

We have included "with altitude"

The reference to the Plumb and Ko paper is certainly valuable, but we note that the curvature plots we show in our paper are the model results, not stratospheric observations to which the Plumb and Ko theory applies. What we discuss here are the deviations from linear relationships as expected from the Plumb and Ko calculations, and we argue that these are artefacts caused by the deficiencies of the box model as explained in the paper.

Referee 2:

We have made clear in the final manuscript, that the isotopic composition of the laboratory reference gas was established on a mass spectrometer at the University of Heidelberg, which is calibrated using the international water standards. As mentioned by the referee, it would be desirable to do the same also for the enriched commercial gases, and we will attempt to do this in the near future. We note, however, that such a calibration versus international standards is also done in the isotope laboratory of the H2 manufacturer who sold us the enriched gases, and we have no reason to doubt these values.

The referee is correct, when the heavy isotopes are concentrated in H2, the light ones must end up as water. We note, however, that since stratospheric water itself is strongly

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depleted in deuterium, the water formed from oxidation of CH4, although depleted relative to the CH4 reactant, will still cause a deuterium enrichment of the water in the stratosphere. We do not investigate the total stratospheric hydrogen isotope balance in this paper, but want to assess this aspect in a future publication.

Regarding a possible influence from higher altitude atmospheric layers, we would like to defer this discussion to a forthcoming publication, because we will soon analyse a set of samples from another balloon flight at high northern latitudes where we suspect mesospheric influence. In such cases the trace gases show some characteristic signatures. SF6 is depleted and the mixing ratios of CO and H2 are much higher than in the mid latitude stratosphere. Such signatures are not observed during the flight presented in this paper. Due to the very low total mass of air in the mesosphere, this process does not influence the mid latitude stratosphere, except under occasions when remnants of the polar vortex are observed in mid- latitudes (e.g. Strunk et al., 2000). In typical mid-latitude conditions, a very good agreement of mean age derived from CO2 and SF6 is found. As SF6 has a sink in the mesosphere, this should not be the case if mesospheric air would generally influence the mid-latitude stratosphere (e.g. Engel et al., 2002).

References:

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Interactive comment on Atmos. Chem. Phys. Discuss., 3, 3745, 2003.