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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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General comments:

The paper by Roeckmann et al. presents new data on the isotopic composition of molecular hydrogen in the stratosphere. In spite of the almost constant mixing ratio as a function of height the deuterium content increases steadily from about 15% above the VSMOW value of 156 ppm at 13 km to more than 40% above 28 km (Fig. 2). The increase correlates linearily with decreasing CH4 (Fig.3). The finding is rather unexpected and requires new interpretation of the role of hydrogen in stratospheric chemistry.

Specific comments:

The measurement of the isotopic composition of hydrogen has become available through an old but wonderful balloon sampling technique involving liquid neon combined with an analysis technique which concentrates H2 on a GC column head prior to GC separation and on-line isotopic analysis. Accuracy of the method has been

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established using commercially available H2 gas with commercially assigned isotopic results. Here, a more direct (VSMOW) assignment using water would have been desirable, although the huge signature may not render this a necessity.

The strong correlation between declining CH4 and increasing D/H suggests exclusive production from CH4. The fractionation is discussed along a pathway involving CH4 oxidation via several steps. Only the final step of formaldehyde oxidation results in H2 production (as well as H2O). However, since all other H ends up in H2O in the stratosphere, it should carry the opposite isotopic signature. The details of the fractionation are not understood, yet, and require further experimental evidence.

Another possible sink of light hydrogen is the preferential loss to outer space. This option is not mentioned in the paper and should be quantified.

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