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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The isotope composition of water vapour: A powerful tool to study transport and chemistry of middle atmospheric water vapour" *by* Ch. Bechtel and A. Zahn

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The paper by Bechtel and Zahn presents a very illustrative model study of the evolution of the isotopic composition of water in the stratosphere and mesosphere. I have a few comments that could be taken into account by the authors to further improve the paper.

General comments

Page 3997: The number of 1.11 for the KIE of CH_4 with $O(^1D)$ does not agree with the value of 1.06 in [Saueressig et al., 2001].

Page 3997: Here or later (section 5), the recent findings of the strong deuterium enrichment of H_2 in the stratosphere [Rahn et al., 2003; Röckmann et al., 2003] and the

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possible effect on the model results should be discussed, as pointed out by one of the referees.

Page 4000, line 17: The isotopic composition of $O(^3P)$ is not the same as that of O_2. Although exchange is indeed rapid, there is a the strong equilibrium fractionation between O and O_2 (e.g. Johnston et al., JGR, 115, D12, 2000). This leads to a strong depletion of oxygen atoms relative to molecules, which has to be included in the model.

Page 4005, middle: Is it possible that hydrogen from CH_4 oxidation is stored in short-lived species for long enough that it can cause a shift in the region of major CH_4 loss and H_2 production of 5 km? I find it hard to believe this explanation. The intermediate species (except for H_2 and HCl) have a short life time and low concentration, so it is unlikely that hydrogen could be stored in these species for such a long time. In any case, the additional hydrogen should show up in other species in the model, and the authors should be able to find out where and whether it is reasonable.

Page 4005, middle: If the chemical lifetime of H_2O is long, it is long, and this should have similar effects on the hydrogen and oxygen isotopic composition. This may be a misunderstanding, then it should be clarified. However, as I understand it, the cause for the different behaviour is not the chemical lifetime of water. What is different is that when water reacts and hydrogen and oxygen are transferred into other reactive compounds, the hydrogen stays in a closed cycle and eventually forms water again, whereas the oxygen in those chemically reactive intermediates exchanges with O_2 and O_3.

Page 4005/4006: As mentioned by one referee, the concept of a mass weighted isotopic composition for the entire middle atmosphere is more confusing than enlightening in this discussion. Since it has no practical significance for any exchange process, I suggest to cut this part.

Page 4006: It should be noted that the 40% contribution from CH_4 can probably also be derived simply from the change in water mixing ratio, and does not necessarily require

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isotope data.

Page 4006/4007: It is not clear to me why the fractionation in CH_4 removal reactions is initially excluded. Apparently it is not a big problem to include this fractionation, which is now well established [McCarthy et al., 2003; Rice et al., 2003], because later the authors make a sensitivity test and show that it only has a small effect. So it could be included from the beginning.

Page 4009: Is the "oxygen isotope exchange" in R35 really exchange of an oxygen atom or rather transfer of the hydrogen atom from HO_2 to O_2?

Page 4009, line 9: Is there anything known about intramolecular exchange of the hydrogen atom in HO_2, i.e. displacement from one end to the other? If so, this could have a tremendous effect, since in this case a new OH bond would be formed.

Page 4010, bottom: In this case, H_2O does not need to have the same isotopic composition as O_2, but it will be in some kind of isotope exchange equilibrium with O_2, as pointed out in my comment above for $O(^3P)$.

Page 4013, line 4/5: As mentioned above, the long chemical life time alone should have a similar effect on both hydrogen and oxygen isotopes.

Minor points

Page 3992, line 14: State in the abstract the region where these overall increases are modelled (from where to where)?

Page 3993, line 19: the value for $R_{D,V-SMOW}$ is 155.76*10^{-6}, the number in the paper is the ratio HDO/H_2O, which is not R_D

Page 3998 line 2: At this point it is not clear what the "MIF signal originating from CH_4 oxidation alone" is. In the previous section on CH_4 oxidation, only D is dealt with.

Page 3998, line 6: "the affection of MIF enriched O_3 to OH..." is not clear. The authors probably mean "transfer ... to OH", or "effect ... on OH"

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Page 4001, line 9: "...calculated from the reduced masses (section 4.3)"

Page 4007: A statement that also mixing decreases gradients could be added in the first paragraph.

Page 4009: Arrow missing in R29

References

McCarthy, M.C., Boering, K.A., Rice, A.L., Tyler, S.C., Connell, P., and Atlas, E.: Carbon and hydrogen isotopic compositions of stratospheric methane: 2. Two-dimensional model results and implications for kinetic isotope effects, Journal of Geophysical Research-Atmospheres, 108, doi:10.1029/2002JD003183, 2003.

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Saueressig, G., Crowley, J.N., Bergamaschi, P., Brühl, C., Brenninkmeijer, C.A.M., and Fischer, H.: Carbon 13 and D kinetic isotope effects in the reactions of CH_4 with $O(^1D)$ and OH: New laboratory measurements and their implications for the isotopic composition of stratospheric methane, J. Geophys. Res., 106, 23127-23138, 2001.

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