

Interactive comment on “A consistent molecular hydrogen isotope chemistry scheme based on an independent bond approximation” by G. Pieterse et al.

Anonymous Referee #3

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general comments: The manuscript by Pieterse, Krol, and Rockmann describes a comprehensive probabilistic approach to understanding hydrogen isotope fractionation in the hydrocarbon oxidation chain resulting in H₂. The topic stems from the chemistry-based deuterium enrichment of atmospheric H₂ from hydrocarbon oxidation which has been observed for more than a decade now. It is of scientific curiosity and of societal importance and will be of interest to scientific readers of ACP. The study is of high scientific quality and manuscript well written. I recommend this manuscript for immediate online review by ACP.

specific comments: Their novel approach uses the phenomenological observation

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that hydrogen kinetic isotope effects in reactions of singly substituted molecules (e.g., $\text{CH}_3\text{D}+\text{OH}$) approach the rate of a molecule that has been substituted with an unreactive functional group (e.g., $\text{CH}_3\text{X}+\text{OH}$, smaller by $\sim 25\%$). (For completeness, authors do include the large primary isotope effect of abstraction of the deuterium species). This semi-empirical probabilistic work is a much more detailed and rigorous in nature than what has come before (Gerst and Quay, 2001; Rhee et al., 2007; Fielberg et al., 2007). Only a true quantum mechanical-based molecular dynamic study would be more fundamental, but these have not proven better in recent past and would be computationally challenging, if possible at all. Though there are numerous assumptions and limits to their method (e.g., secondary KIEs), authors are careful to point these out within the manuscript. In the absence of real kinetic isotope effect measurements of all individual steps in the reaction sequence, I believe this to be the most robust current approach for understanding (and precursors) deuterium enrichment of H_2 through atmospheric processes. After developing their probabilistic method, authors then employ a simple atmospheric box model to test their isotope chemistry, which does a reasonable job simulating the deuterium enrichment of CH_2O and H_2 , a priori. The atmospheric model, in turn, elucidates important sensitivities to assumptions of the chemical isotope scheme. It is also able to identify largest uncertainties and areas of future scientific focus.

With the overall high quality of the study in mind, there are a few manuscript features that could be improved. Most importantly, the approach put forth by Pieterse et al. is very involved and has a number of assumptions. The result is a somewhat cumbersome solution that is of unsatisfying complexity. The authors have done a good job of presenting the material in a palatable manner (manuscript is carefully written), but ultimately the complexity of the model will leave many readers bogged down in details or lost completely, I fear. For this reason, I recommend a discussion summary (either in section 4 or 5) which outlines the most critical sensitivities and uncertainties which were identified through implementation of the reaction chemistry scheme with the box model. For example, which reaction steps have the most leveraging effect on

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the isotopic composition of H₂? Based on my read of the manuscript, it appears the deuterium content of CH₂O is critical and that it is the photolysis effect which has the largest impact on the D/H ratio in CH₂O and H₂. Similarly, which assumptions are most sensitive to and impact the deuterium content of H₂ the most?

technical corrections/comments: Lines 93-103: The differentiation between MIE and KIE is still confusing. Were it not for the large hydrogen primary KIE, the MIE would not exist – its not a purely ‘counting issue’. Because the crux of the study relies on readers understanding this differentiation here, I suggest re-wording this paragraph carefully for clarity.

Table 4: Use of -628 permil from soil N₂ fixation is probably erroneous. Though in the ocean H₂ will equilibrate with H₂O giving the low D/H ratio, the oxidation of H₂ produced in the soils through N₂ fixation will almost certainly enrich deuterium in H₂ relative to source H₂. Unfortunately, there is not published value to use in its place. Because of the leveraging effect at -628 (even at 4% of the budget), I would leave this term out of the isotope budget.

Table 5: Based on the table caption, I would expect that the value for H₂ would reflect the photochemical source (+95?), not the isotopic mass balance (+64).

Lines 449-451: This sentence is confusing

Lines 482-485: Poorly constructed sentence

Lines 531-536: Unclear paragraph. What is being said here about the Fielberg study and the photochemical source?

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 5679, 2009.

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