

Review of Joelsson et al

The isotopic “clumping” in molecules of atmospheric gases, including methane, is currently seen as an additional and potentially powerful tool to disentangle their often complicated budgets. In order to use this clumping as additional information in budget studies, the signature of the main sources and sinks must be known. Here is where the present paper contributes, by characterizing the KIE of the reaction $^{13}\text{CH}_3\text{D} + \text{OH}$ over the temperature range 278 to 313K. This study is important because the reaction with OH is responsible for the largest sink of atmospheric methane, and this clumped KIE has not been studied. The paper is very relevant for atmospheric methane, and well within the ACP scope.

The paper is overall well-structured and concise. In my opinion, some parts need to include more information (see specific comments) and the relevance for the atmospheric methane needs to be discussed. I recommend publication with minor revision, after the comments below have been taken into account.

Specific comments

1. I find the title a bit misleading; consider removing the first part of the title.
2. page 27854 lines 11 – 13: I think the phrase starting with “ We find” is not completely correct. The values mentioned here for the k ratios do not imply just by themselves that the $\text{CH}_4 + \text{OH}$ KIE is multiplicative, but only when a value for $k_{\text{CH}_4} / k^{13}\text{CH}_4$ of about 1 is considered. Please consider changing the phrase to include this. The same comment for the similar phrase in Conclusions.
3. Section 2.2 is called “Photoreactor”, but it only describes the reactor in the first paragraph; the rest of the subsection describes the actual experiments. I suggest splitting this subsection in two, such that the experiments are described separately.
4. page 27858 lines 16 – 17: “all at the concentrations given in Table 3” – I could not find the concentrations for all the listed species in Table 3, but only for O_3 . The text here could be corrected, but I actually think that it would be useful to give these (starting) concentrations in Table 3.
5. In Sect 2.2 it is described how O_3 is produced and then photolyzed to $\text{O}(\text{D}) + \text{O}_2$, but the experiments should actually be on the $\text{CH}_4 + \text{OH}$ reaction. Is it possible that some part went missing, the one that would describe how the OH is obtained and how the reaction with CH_4 takes place? Please add this information, in the current form it is not clear how the OH is obtained, and what the connection is between O_3 and the purpose of this paper.
6. I suggest to include in the beginning of Sect 2 (before 2.1) or in the beginning of 2.2 a short overview of the experiments that have been done (one phrase) and already send to Table 3. In Sect 2.2 (page 27858 line 7) when the specifier “Experiments 1-4” appears, the reader should already know that these exist.
7. I suggest that the tables should be reordered, with the one that is now Table 3 moved in front at “Table 1”
8. page 27858 lines 6 – 8: why were two detectors used?

9. page 27860 lines 2 – 4: I find this phrase unclear. If I understand correctly, the $^{13}\text{CH}_3\text{D}$ is calculated from the 2140 – 2302 region, then the concentration calculated there is used to simulate the $^{13}\text{CH}_3\text{D}$ spectrum in the 2850 – 3009 region, which is then used to correct the $^{12}\text{CH}_4$ spectrum in the region 2850 – 3009, and from this the $^{12}\text{CH}_4$ concentration. If my understanding is correct, please consider reformulating / clarifying the corresponding phrase in the paper.

10. page 27860 line 15: unclear, how is the fitting method of York et al adjusted?

11. page 27860 lines 16 – 20: I find this temperature description difficult to follow and I'm not sure I understand it correctly. Do you mean that, for each experiment, you take the average of the two sensors' measurements over time, and the uncertainty is the stdev of all measurements? Please consider reformulating this part.

12. page 27860, Sect. 2.4: please consider including an explanatory phrase in the beginning of this section, something like: "a kinetic model was used for ..." followed by the purpose of this exercise.

13. page 27861, line 14: Please specify whether a correction for the reaction with O1D has been performed on the final $\text{CH}_4 + \text{OH}$ results, or not.

14. page 27861 lines 13- 14: the text here is unclear. The loss to O1D is estimated based on N_2O at 2.3%. Then "the model" gives 4.7%, but it is unclear, which model is this? Is it the one that was used above, and it gave 4.4% (see line 5)? Please clarify this part in the paper.

15. page 27863 line 10: the error for $^{13}\text{C,D}\alpha$ is given as 0.01. Where is this coming from? If it is the stdev of the two values from experiments 9 and 10, then the number is not correct. Please verify and change if needed. Also, please adjust the error for γ_{exp} correspondingly.

16. I find the discussion and conclusion parts a bit too short. In particular, I think a discussion on the implications for the atmospheric CH_4 and for the possibility to use clumped isotopes to constrain its budget is missing. For example, would a non-existent or very small clumped isotope effect in the $\text{CH}_4 + \text{OH}$ reaction, given that this is the main sink for CH_4 , improve the chances to follow the sources based on their clumped signatures? Please consider adding such a discussion, which would show the relevance of the results presented here for atmospheric CH_4 .

Minor and technical comments

page 27854 line 8: it is stated here that the oxidation by OH accounts for "around 90% of methane removal"; in the Introduction (page 27855, line 6) the OH oxidation in the troposphere is given as 84%. These are not consistent; I suggest changing the number in the abstract to 84%.

page 27854 line 14: typo "the kinetic isotope effect were" → either "was" or "effects"

page 27854 line 17: typo "the isotope effects is" → either "effect" or "are"

page 27854 line 24: either typo or something missing: "forcing of methane **from is ...**"

page 27860 line 15: typo, "is used" should be "are used"

page 27860 line 15: typo, “are adjusted” should be “is adjusted”

page 27861 line 2: “with experiment” – do you mean “during the experiment”, or “ from one experiment to the next”? Please clarify in the paper.

page 27861 lines 2 – 3: the phrase starting with “The model” seems incomplete.

page 27864 line 3: I suggest mentioning again the value for the room temperature $^{13}\text{C}, \text{D} \alpha$

page 27864 lines 8 – 11: the phrase starting with “The $\text{D} \alpha$ value...” does not seem to belong here, maybe moved by mistake from a paragraph above?