

***Interactive comment on* “Development of a new methane tracer: kinetic isotope effect of $^{13}\text{CH}_3\text{D} + \text{OH}$ from 278 to 313 K” by L. M. T. Joelsson et al.**

L. M. T. Joelsson et al.

joelsson@chem.ku.dk

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To the editorial office,

On behalf of all co-authors and myself, I hereby submit a revised version of our manuscript “Kinetic isotope effects in $^{12}\text{CH}_3\text{D} + \text{OH}$ and $^{13}\text{CH}_3\text{D} + \text{OH}$ from 278 to 313 K” (originally “Development of a new methane tracer: kinetic isotope effect of $^{13}\text{CH}_3\text{D} + \text{OH}$ from 278 to 313 K”) We thank the three reviewers for carefully reading our manuscript and providing us with valuable feedback for improving the manuscript. We copy below the reviewer comments and a point-by-point response including all implemented changes to the original manuscript.

Sincerely,

Magnus Joelsson

Reviewer 2:

1. **Comment:** “I find the title a bit misleading; consider removing the first part of the title.”

Response: Title is changed to: “Kinetic isotope effects in $^{12}\text{CH}_3\text{D} + \text{OH}$ and $^{13}\text{CH}_3\text{D} + \text{OH}$ from 278 to 313 K”

2. **Comment:** 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.”

Response: It is added that “ $k(\text{CH}_4)/k(^{13}\text{CH}_4) = 1.0039$ ” in the Conclusion and in the Abstract.

3. **Comment:** “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.”

Response: The subsection “2.3 Laboratory procedure” is added to the manuscript

4. **Comment:** “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

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O₃. The text here could be corrected, but I actually think that it would be useful to give these (starting) concentrations in Table 3.”

Response: The methane, ozone, and water starting concentrations are now given in Table 1.

5. **Comment:** “In Sect 2.2 it is described how O₃ is produced and then photolyzed to O¹D + O₂, but the experiments should actually be on the CH₄ + 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 CH₄ 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 O₃ and the purpose of this paper.”

Response: Reaction (R7) “O(1D) + hν → OH + OH” is added.

6. **Comment:** “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.”

Response: A short experimental overview is added (Sect. 2): “Sixteen experiments were conducted, numbered from 1 through 16, see Table 1; eight (Experiments 1-8) for ¹²CH₃D and eight (Experiments 9-16) for ¹³CH₃D. The experiments were conducted at four different temperatures ($T = [298, 278, 288, 313]K = [25, 5, 15, 40]^\circ C$); two experiments were conducted for each temperature.”

7. **Comment:** “I suggest that the tables should be reordered, with the one that is now Table 3 moved in front at ‘Table 1’”

Response: The Tables are ordered such that Table 1, 2, and 4 is now Table 3:5, Table 3 is split up in Table 1 and Table 2

8. **Comment:** “page 27858 lines 6–8: why were two detectors used?”

Response: The following sentence is added: “the MCT-detector is used in Experiments 1-4 for logistical reasons”

9. **Comment:** “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.”

Response: The passage is changed to: “The concentrations of $^{12}\text{CH}_3\text{D}$ and $^{13}\text{CH}_3\text{D}$ were calculated from spectral fits in the region 2140–2302 cm^{-1} , see Fig. 1 and 2. Interference from H_2O , CO_2 , and CO was eliminated by including simulated spectra obtained from the HITRAN database in the fit. As there is no HITRAN data available for $^{13}\text{CH}_3\text{D}$ in this region, the cross sections from 2000–2400 cm^{-1} for this isotopologue were estimated by shifting the spectrum of $^{12}\text{CH}_3\text{D}$, see Joelsson et al. (2014). Concentrations of $^{12}\text{CH}_4$ were calculated from spectral fits in the region 2838–2997 cm^{-1} . Interference from $^{13}\text{CH}_3\text{D}$ was reduced by including temperature adjusted reference spectra in the fit, and interference from $^{12}\text{CH}_3\text{D}$, H_2O , and H_2CO was by including simulated spectra obtained from the HITRAN database in the fit, see Fig. 3. The spectral windows were sometimes adjusted to exclude saturated lines.”

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

Response: The following sentence is added: “In the temperature dependence curve fitting procedure, the parameters A and B are from a linearized version of the Arrhenius equation: [...] are adjusted to match experimental. Also here, the method of York et al. (2004) was used.”

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11. **Comment:** “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.”

Response: These lines are reformulated as: “The temperature in the cell was taken as the spatial average of the measurements from two thermocouples inside the temperature housing. The experiment temperature was defined by the temporal mean of the spatially averaged temperature measurement series and the uncertainty of the experiment temperature was the standard deviation of the spatially averaged temperature measurement series.”

12. **Comment:** “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.”

Response: The following sentence is added in Sect. 2.5: A kinetic model was used to determine the influence of $O(^1D)$, reaction (R3), which rivals reaction (R1).

13. **Comment:** “page 27861, line 14: Please specify whether a correction for the reaction with $O(^1D)$ has been performed on the final $CH_4 + OH$ results, or not.”

Response: The following sentence is added: “No correction is applied, and the possible deviation is included in the estimated error.”

14. **Comment:** “page 27861 lines 13- 14: the text here is unclear. The loss to $O(^1D)$ 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.”

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Response: 4.7 % is for the additional experiment, 4.4 % is for Experiment 2, this is clarified by the sentence: “The kinetic model described above estimated that 4.7 % [CH₄] were lost by Reaction (R3) for this additional experiment.”

15. **Comment:** “page 27863 line 10: the error for ¹³C, D_α 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.”

Response: This was a misprint: The uncertainty is 0.03 for $k(\text{CH}_4)/k(^{13}\text{CH}_3\text{D})$

16. **Comment:** “I find the discussion and conclusion parts a bit too short. In particular, I think a discussion on the implications for the atmospheric CH₄ 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 CH₄ + OH reaction, given that this is the main sink for CH₄, 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 CH₄.”

Response: An Atmospheric implication section is added: “At steady state, assuming no clumping in emissions, $\Delta(^{13}\text{CH}_3\text{D}) = \ln(\gamma)$. It follows that $\Delta(^{13}\text{CH}_3\text{D}) = 0.02 \pm 0.02$ implying that the clumped isotope effect of the OH reaction is very small. In turn, this implies that the bulk tropospheric $\Delta(^{13}\text{CH}_3\text{D})$ reflects the source signal with relatively small adjustment due to the sink signal (i.e. mainly OH). $\Delta(^{13}\text{CH}_3\text{D})$ would therefore be a more straightforward tracer for tracking methane sources than conventional isotopic analysis. However, the present uncertainty overrides the current estimated methane source signals (Wang et al. 2015), thus more precise measurements are necessary.”

17. **Comment:** Minor comments

Response: The manuscript should be change according to all minor comments
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References

York et al., Unified equations for the slope, intercept, and standard errors of best straight line, *Am. J. Phys.*, 72, 3, 367–375, 2004.

Wang et al., Nonequilibrium clumped isotope signals in microbial methane, *Science*, 348, 6233, 428–431, 2015.

[Interactive comment on Atmos. Chem. Phys. Discuss.](#), 15, 27853, 2015.

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Table 1. Experimental setup. The experiment numbers are listed in column Exp., the detector in the column Detect., the heavy CH₄ isotopologue included in the experiments are listed in column [^xCH₃D], the mean measured temperatures in the photoreactor are listed in column *T*, the H₂O-vapour concentrations at the start of the experiments (*t* = 0) as obtain from spectral fitting are listed in column [H₂O]_{*t*=0}, the mean O₃ concentration after refill (i.e. the “top”-values) as obtain from spectral fitting are listed in column [O₃]_{*t*top}, the ¹²CH₄- concentrations at the start of the experiments (*t* = 0) as obtain from spectral fitting are listed in column [¹²CH₄]_{*t*=0}, and the heavy CH₄ concentrations at the start of the experiments (*t* = 0) as obtain from spectral fitting are listed in column [^xCH₃D]_{*t*=0}. Note that for the experiment including CH₃D, the value of initial concentration only refers to [¹²CH₃D]_{*t*=0}.

Exp.	Detect.	^x CH ₃ D	<i>T</i> K	[H ₂ O] _{<i>t</i>=0} hPa	[O ₃] _{<i>t</i>top} hPa	[¹² CH ₄] _{<i>t</i>=0} hPa	[^x CH ₃ D] _{<i>t</i>=0} hPa
1	MCT	CH ₃ D	298.2 ± 1.2	7.1	– ^a	0.030	0.054
2	MCT	CH ₃ D	297.6 ± 0.8	5.6	0.19	0.058	0.042
3	MCT	CH ₃ D	277.2 ± 0.2	5.2	0.29	0.109	0.046
4	MCT	CH ₃ D	277.0 ± 0.2	5.1	0.16	0.073	0.035
5	InSb	CH ₃ D	284.5 ± 0.1	7.2	0.26	0.025	0.033
6	InSb	CH ₃ D	291.1 ± 0.2	7.4	– ^a	0.052	0.050
7	InSb	CH ₃ D	313.5 ± 1.3	7.1	0.17	0.025	0.029
8	InSb	CH ₃ D	312.4 ± 0.9	4.3	– ^a	0.022	0.040
9	InSb	¹³ CH ₃ D	298.5 ± 0.1	5.1	– ^a	0.035	0.026
10	InSb	¹³ CH ₃ D	297.6 ± 0.6	6.4	0.13	0.025	0.033
11	InSb	¹³ CH ₃ D	276.8 ± 0.8	5.4	– ^a	0.024	0.024
12	InSb	¹³ CH ₃ D	277.2 ± 1.3	5.1	– ^a	0.022	0.030
13	InSb	¹³ CH ₃ D	287.4 ± 1.2	5.4	– ^a	0.021	0.028
14	InSb	¹³ CH ₃ D	287.4 ± 0.4	4.5	– ^a	0.016	0.029
15	InSb	¹³ CH ₃ D	314.4 ± 1.0	5.2	0.26	0.023	0.037
16	InSb	¹³ CH ₃ D	313.8 ± 0.8	8.3	0.17	0.025	0.035

^aSpectra recorded during or after photolysis, [O₃]_{*t*top} not available

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