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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Development of a new methane tracer: kinetic isotope effect of $^{13}CH_3D$ + OH from 278 to 313 K" *by* L. M. T. Joelsson et al.

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1. I find the title a bit misleading; consider removing the first part of the title. Response: Title is changed to: Kinetic isotope effects in 12CH3D + OH and 13CH3D + OH from 278 to 313 K 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 CH4 + OH KIE is multiplicative, but only when a value for kCH4 /k13CH4 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(CH4)/k(13CH4)=1.0039 in the Conclusion and in the Abstract 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

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two, such that the experiments are described separately. Response: The subsection "2.3 Laboratory procedure" is added to the manuscript 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 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. In Sect 2.2 it is described how O3 i 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 $\rightarrow$ OH + OH is added 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. Response: A short experimental overview is added (Sect. 2): Sixteen experiments where 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. 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. 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. page 27860 lines 2 – 4: I find this phrase unclear. If I understand correctly, the 13CH3D is calculated form the 2140 – 2302 region, then the concentration calculated there is used to simulate the 13CH3D spectrum in the 2850 – 3009 region, which is then used to correct the 12CH4 spectrum

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in the region 2850 – 3009, and from this the 12CH4 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 12CH3D and 13CH3D were calculated from spectral fits in the region 2140-2302 cm-1, see Fig. 1 and 2. Interference from H2O, CO2, and CO was eliminated by including simulated spectra obtained from the HITRAN database in the fit. As there is no HITRAN data available for 13CH3D in this region, the cross sections from 2000-2400 cm-1 for this isotopologue were estimated by shifting the spectrum of 12CH3D, see Joelsson et al. (2014). Concentrations of 12CH4 were calculated from spectral fits in the region 2838-2997 cm-1. Interference from 13CH3D was reduced by including temperature adjusted reference spectra in the fit, and interference from 12CH3D, H2O, and H2CO 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. 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. 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. 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. 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:

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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. page 27861, line 14: Please specify whether a correction for the reaction with O1D has been performed on the final CH4 + 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. page 27861 lines 13- 14: the text here is unclear. The loss to O1D is estimated based on N2O 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. 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. page 27863 line 10: the error for 13C,Dα 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 ÏŠexp correspondingly. Response: This was a misprint: The uncertainty is 0.03 for k(CH4)/k(13CH3D) 16. 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. 17. The manuscript should be change according to all minor comments

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/15/C12611/2016/acpd-15-C12611-2016-supplement.pdf

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