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 $^{12}CH_3D$ + OH and $^{13}CH_3D$ + OH from 278 to 313 K” (originally “Development of a new methane tracer: kinetic isotope effect of $^{13}CH_3D$ + 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 (in italic) and a point-by-point response including all implemented changes to the original manuscript (highlighted in yellow).

Sincerely,

Magnus Joelsson

**Reviewer 1:**

1. *Importance of isotope analysis for the atmospheric CH4 tracer? First of all, I do not agree with the title entitled “new atmospheric CH4 tracer”, and this is overselling of this experimental results. The title should be like “Kinetic isotope effect of 13CH3D+OH from 278 to 313K”.*
   **Response:** Title is changed to: Kinetic isotope effects in $^{12}CH_3D$ + OH and $^{13}CH_3D$ + OH from 278 to 313 K.
   *In current manuscript, authors explained a few about the importance for determination of isotopic fractionation in atmospheric methane sink reactions. Based on the previous studies using 13C and D, what do authors expect is main advantage of using clumped CH4 for better understanding of atmospheric methane cycles? In revised manuscript, following points should be addressed. (1) In the introduction, explain a bit more about how conventional isotopic information have helped understanding of atmospheric CH4 cycle. Describe the importance or possibility of the new CH4 tracer of clumped isotope well. How do authors aim to overcome the problems remained using clumped CH4?*
   **Response:** The following sentence is added to the Introduction: Recent advances in mass spectrometry (Eiler et al. 2013; Stolper et al. 2014) and laser infrared spectroscopy (Ono et al. 2014; Wang et al. 2015) facilitate measurement of rare double-substituted isotopologues. The abundance of these “clumped” isotopologues (clumped refers to the rare isotopes being clumped together) generally follows a stochastic distribution (i.e. [$^{12}$CH4][ $^{13}CH_3D$] = [$^{13}CH_4$][ $^{12}CH_3D$]). However, small deviations from stochastic distribution can be induced by thermodynamic (Ma et al. 2008; Stolper et al. 2014; Liu and Liu 2016}, kinetic (Joelsson et al. 2014; Wang et al. 2015), and photolytic processes (Schmidt et al. 2013; Schmidt and Johnson 2015). Analysis of the clumped isotope anomaly in methane will yield unique constraints for the methane budget. Optical methods, as will be shown in this paper, provide high throughput and accuracy for overcoming the problems of analysis of clumped $CH_4$. The difference and advantage of this approach is the additional information not available in single isotope analysis, especially regarding the mechanism of formation, independent of the enrichment of D and $^{13}$C in the starting material. The following additional references is added in the introduction: (Quay et al. 1999; Bergamaschi et al. 2000; Allan et al. 2001a;b)
   *What is the difference (and advantage) from conventional isotopic information of CH4?*

**Response:** $\Delta(^{13}CH_3D)$ offers an additional dimension in the isotopic fractionation space, furthermore a small $\Delta(^{13}CH_3D)$ in the sink would make the tracking of sources using $\Delta(^{13}CH_3D)$ more straight forward than conventional isotope fractionations. See response 2) below.

*(2) According to the results, not significant effects on clumped isotope were observed for CH4 + OH reaction. For this case, readers might not understand the importance of atmospheric clumped CH4. If authors suggest clumped CH4 is nice and new CH4 tracer in the title, I think this is an essential discussion for discussion section.*

**Response:** See response 2)

**2.** *Atmospheric implication Authors should add section of "Atmospheric implication" in discussion. If authors only present the experimental results, and brief discussion of the data, I do not think this paper is suitable for atmospheric chemistry journal like ACP. In revised manuscript, implication for the atmospheric chemistry should be discussed as much as author can. The determined isotopic fractionation for clumped isotope of CH4 enables us to discuss changes in isotopic composition of CH4 in the atmosphere. For example, if authors compare the results obtained in this study with other possible atmospheric reaction, which authors previously determined CH4 + Cl reactions, authors would able to determine atmospheric fractionations. In addition, if expected changes in isotopic compositions for clumped isotope in the atmosphere are small for the sink reactions, the atmospheric clumped isotope of CH4 could still preserve the source information. This is nice and new tool to reconstruct source budget without any influences from sink reactions. Authors should add some interpretation and/or implication for atmosphere using investigated isotopic fractionation.*

**Response:** The "4.1 Atmospheric implication" section is added: At steady state, assuming no clumping in emissions, $\Delta(^{13}CH_3D) = \ln(\gamma)$. It follows that $\Delta(^{13}CH_3D) = 0.02 \pm 0.02$ implying that the clumped isotope effect of the OH reaction is very small. In turn, this implies that the bulk tropospheric $\Delta(^{13}CH_3D)$ reflects the source signal with relatively small adjustment due to the sink signal (i.e. mainly OH). $\Delta(^{13}CH_3D)$ 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.

3. *Data analysis is poorly described Authors explained very few for the data analysis and did not show raw data sets for the chamber experiments. First, as presented Figs S2-S4, the spectrum of measured, fitted and residuals should be presented in the main manuscript (not in the supporting information). If it is possible, the reference spectrum for CH4 isotopologues and O3 help reader's understanding. Second, the spectrum fitting is one of the important possible errors in this relative rate plot method. Please explain well about the errors budget for each concentrations of CH4 and its isotopologues for fitting calculation. For Fig S1, authors plotted the data without error bar for single calculation of MALT in current manuscript, but I think authors should add the error bar in all plots on the basis of calculation from MALT. I recommend to additional sub-section of data analysis for results, and then start discussion of isotope effect, and implication as I have already recomended.*

**Response:** Figures 1-3 show the measured, key reference spectra, and the residual between the two for an example experiment. The error bars are included in the relative rate plots, but they are almost too small to see. The "2.4 Data analysis" sub-section is added. The following sentence is added in Sect. 2.4 to improve the description of the data analysis: The experimental IR spectra were analyzed using the program MALT which simulates experimental FTIR spectra (Griffith et al. 1996) combined with non-linear least squares fitting to best-fit the calculated spectra to measured spectra (Griffith et al. 2012).

4. *(k(CH4)/k(13CH4))(kCH4/kCH3D) = k(CH4)/k(13CH3D) is difficult to be understood, because no information for kCH4/k13CH4 were not presented. P27858 L1 The experimental section should be written in the past tense. This correction should be applied throughout this manuscript.*
   **Response:** The sentence: given the literature value of $k(CH_4)/k(^{13}CH_4)=1.0039\pm0.0002$ is added to the Abstract and the experimental part is changed to past tense.

**Reviewer 2:**

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 $^{12}CH_3D$ + OH and $^{13}CH_3D$ + 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 $k(CH_4)/k(^{13}CH_4)=1.0039$ 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 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) $O(^1D) + h\nu \rightarrow OH + OH$ 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 $^{12}CH_3D$ and eight (Experiments 9-16) for $^{13}CH_3D$. The experiments were conducted at four different temperatures ($T$=[298, 278, 288, 313] K=[25, 5, 15, 40] °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 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 $^{12}CH_3D$ and $^{13}CH_3D$ 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 $^{13}CH_3D$ in this region, the cross sections from 2000-2400 cm$^{-1}$ for this isotopologue were estimated by shifting the spectrum of $^{12}CH_3D$, see Joelsson et al. (2014). Concentrations of $^{12}CH_4$ were calculated from spectral fits in the region 2838-2997 cm$^{-1}$. Interference from $^{13}CH_3D$ was reduced by including temperature adjusted reference spectra in the fit, and interference from $^{12}CH_3D$, $H_2O$, 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. *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:** The following sentence is added in Sect. 2.5: A kinetic model was used to determine the influence of O($^1$D), 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 % [$CH_4$] 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 ϒexp correspondingly.*
**Response:** This was a misprint: The uncertainty is 0.03 for $k(CH_4)/k(^{13}CH_3D)$
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

Eiler, John M., et al. "A high-resolution gas-source isotope ratio mass spectrometer." International Journal of Mass Spectrometry 335 (2013): 45-56.

Stolper, D. A., et al. "Combined 13 C–D and D–D clumping in methane: Methods and preliminary results." Geochimica et Cosmochimica Acta 126 (2014): 169-191.

Ono, Shuhei, et al. "Measurement of a doubly substituted methane isotopologue, 13CH3D, by tunable infrared laser direct absorption spectroscopy." Analytical chemistry 86.13 (2014): 6487-6494.

Wang, David T., et al. "Nonequilibrium clumped isotope signals in microbial methane." Science 348.6233 (2015): 428-431.

Ma, Qisheng, Sheng Wu, and Yongchun Tang. "Formation and abundance of doubly-substituted methane isotopologues (13 CH 3 D) in natural gas systems." Geochimica et Cosmochimica Acta 72.22 (2008): 5446-5456.

Liu, Qi, and Yun Liu. "Clumped-isotope signatures at equilibrium of CH 4, NH 3, H 2 O, H 2 S and SO 2." Geochimica et Cosmochimica Acta 175 (2016): 252-270.

Joelsson, Lars Magnus Torvald, et al. "Relative rate study of the kinetic isotope effect in the 13 CH 3 D+ Cl reaction." Chemical Physics Letters 605 (2014): 152-157.

Schmidt, Johan A., Matthew S. Johnson, and Reinhard Schinke. "Carbon dioxide photolysis from 150 to 210 nm: Singlet and triplet channel dynamics, UV-spectrum, and isotope effects." Proceedings of the National Academy of Sciences 110.44 (2013): 17691-17696.

Schmidt, Johan A., and Matthew S. Johnson. "Clumped isotope perturbation in tropospheric nitrous oxide from stratospheric photolysis." Geophysical Research Letters 42.9 (2015): 3546-3552.

Quay, Paul, et al. "The isotopic composition of atmospheric methane." Global Biogeochemical Cycles 13.2 (1999): 445-461.

Bergamaschi, Peter, et al. "Measurements of the carbon and hydrogen isotopes of atmospheric methane at Izaña, Tenerife: Seasonal cycles and synoptic-scale variations." Journal of Geophysical Research: Atmospheres 105.D11 (2000): 14531-14546.

Allan, W., D. C. Lowe, and J. M. Cainey. "Active chlorine in the remote marine boundary layer: Modeling anomalous measurements of δ13C in methane." Geophysical research letters 28.17 (2001a): 3239-3242.

Allan, W., et al. "Modeling the variation of δ13C in atmospheric methane: Phase ellipses and the kinetic isotope effect." Global biogeochemical cycles 15.2 (2001): 467-481.

Griffith, David WT. "Synthetic calibration and quantitative analysis of gas-phase FT-IR spectra." Applied spectroscopy 50.1 (1996): 59-70.

Griffith, D. W. T., et al. "A Fourier transform infrared trace gas and isotope analyser for atmospheric applications." Atmospheric Measurement Techniques 5.10 (2012): 2481-2498.

York, Derek, et al. "Unified equations for the slope, intercept, and standard errors of the best straight line." American Journal of Physics 72.3 (2004): 367-375.