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 and a point-by-point response including all implemented changes to the original manuscript.

Sincerely,

Magnus Joelsson

Reviewer 1:

1. **Comment:** "Importance of isotope analysis for the atmospheric CH_4 tracer? First of all, I do not agree with the title entitled 'new atmospheric CH_4 tracer', and this is overselling of this experimental results. The title should be like 'Kinetic isotope effect of $^{13}CH_3D + OH$ 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."

   Comment: "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 ^{13}C and D, what do authors expect is main advantage of using clumped CH_4 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 CH_4 cycle. Describe the importance or possibility of the new CH_4 tracer of clumped isotope well. How do authors aim to overcome the problems remained using clumped CH_4?"

   Response: The following sentence is added to the Introduction: "Recent advances in mass spectrometry [1, 2] and laser infrared spectroscopy [3, 4] 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. $[^{12}CH_4][^{13}CH_3D] = [^{13}CH_4][^{12}CH_3D]$). However, small deviations from stochastic distribution can be induced by thermodynamic [5, 2, 6], kinetic [7, 4], and photolytic processes [8, 9]. 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: "Thus, the construction of an accurate top-down methane budget by isotopic analysis, must take the isotopic signatures of both sources and sinks into account [10, 11, 12, 13]."

Comment: "What is the difference (and advantage) from conventional isotopic information of CH_4?"

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.

Comment: "(2) According to the results, not significant effects on clumped isotope were observed for $CH_4 + OH$ reaction. For this case, readers might not understand the importance of atmospheric clumped CH_4. If authors suggest clumped CH_4 is nice and new CH_4 tracer in the title, I think this is an essential discussion for discussion section."

Response: See response 2

2. **Comment:** "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 CH_4 enables us to discuss changes in isotopic composition of CH_4 in the atmosphere. For example, if authors compare the results obtained in this study with other possible atmospheric reaction, which authors previously determined CH_4 + 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 CH_4 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 track-

ing methane sources than conventional isotopic analysis. However, the present uncertainty overrides the current estimated methane source signals [4], thus more precise measurements are necessary."

3. **Comment:** "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 CH_4 isotopologues and O_3 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 CH_4 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, 2, and 3 (attached) 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 [14] combined with non-linear least squares fitting to best-fit the calculated spectra to measured spectra [15]."

4. **Comment:** "$(k(CH_4)/k(^{13}CH_4))(kCH_4/kCH3D) = k(CH_4)/k(^{13}CH_3D)$ is difficult to be understood, because no information for $kCH_4/k\ ^{13}CH_4$ 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 $k(CH_4)/k(^{13}CH_4) = 1.0039 \pm 0.0002$" is added to the Abstract and the experimental part is changed to past tense.

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 $^{12}CH_3D + OH$ and $^{13}CH_3D + OH$ 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 $CH_4 + OH$ KIE is multiplicative, but only when a value for $kCH_4/k^{13}CH_4$ 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 "$k(CH_4)/k(^{13}CH_4) = 1.0039$" 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 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."

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

5. **Comment:** "In Sect 2.2 it is described how O_3 i produced and then photolyzed to $O^1D + O_2$, but the experiments should actually be on the $CH_4 + OH$ 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."

   Response: Reaction (R7) "$O(1D) + h\nu \rightarrow OH + OH$" 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 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. **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 $^{13}CH_3D$ is calculated form the 2140–2302 region, then the concentration calculated there is used to simulate the $^{13}CH_3D$ spectrum in the 2850–3009 region, which is then used to correct the $^{12}CH_4$ spectrum in the region 2850–3009, and from this the $^{12}CH_4$ 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 $^{12}CH_3D$ 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. **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."

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

    Response: 4.7

15. **Comment:** "page 27863 line 10: the error for ^{13}C, 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 $\check{D}$'exp correspondingly."

    Response: This was a misprint: The uncertainty is 0.03 for $k(CH_4)/k(^{13}CH_3D)$

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 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 $CH_4 + OH$ 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."

    Response: An 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

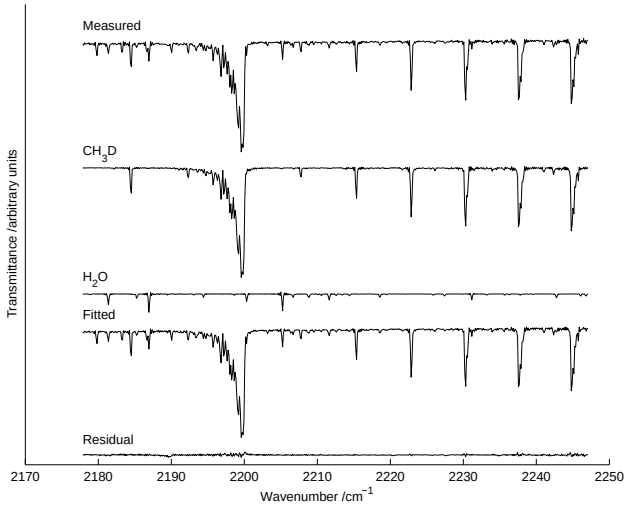

Figure 1: A typical spectral fit in the region where [$^{12}CH_3D$] is obtained (Experiment 5). Experimental data are shown by the topmost line, followed by the fitted (synthetic) partial spectra of the most dominant absorbers (CH_3D and H_2O), the resulting fitted (synthetic) spectrum (also including CO_2 and CO), and the residual between the measured and fitted spectra is shown by the bottom line.

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 [4], thus more precise measurements are necessary."

17. **Comment:** Minor comments

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

References

[1] Eiler et al., A high-resolution gas-source isotope ratio mass spectrometer, International Journal of Mass Spectrometry, 335, 45–56, 2013.

[2] Stolper et al., Combined C-13-D and D-D clumping in methane: Methods and preliminary results, Geochimica Et Cosmochimica Acta, 126, 169–191, 2014.

[3] Ono et al., Measurement of a Doubly Substituted Methane Isotopologue, $^{13}CH_3D$, by Tunable Infrared Laser Direct Absorption Spectroscopy, Analytical chemistry, 86, 13, 6487–6494, 2014.

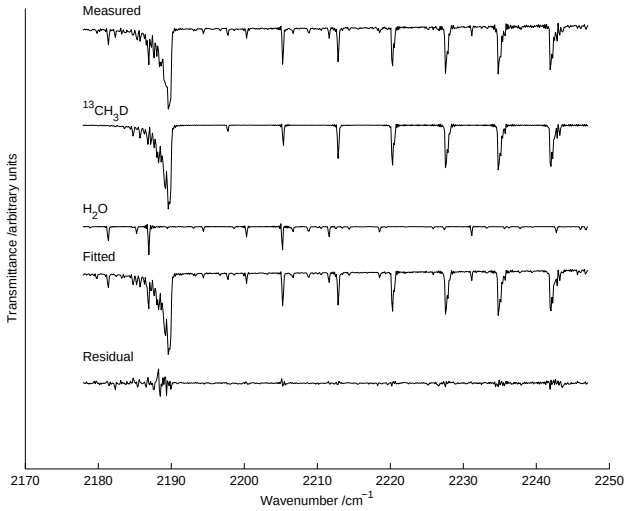

Figure 2: A typical spectral fit in the region where [$^{13}CH_3D$] is obtained (Experiment 10). Experimental data are shown by the topmost line, followed by the fitted (synthetic) partial spectra of the most dominant absorbers ($^{13}CH_3D$ and H_2O), the resulting fitted (synthetic) spectrum (also including CO_2 and CO), and the residual between the measured and fitted spectra is shown by the bottom line.

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

[5] Ma et al., Formation and abundance of doubly-substituted methane isotopologues ($(CH_3D) - C - 13$) in natural gas systems, Geochimica et Cosmochimica Acta, 72, 22, 5446–5456, 2008.

[6] , Liu and Liu, Clumped-isotope signatures at equilibrium of CH_4, NH_3, H_2O, H_2S and SO_2, Geochimica et Cosmochimica Acta, 175, 252–270, 2016.

[7] Joelsson et al., Relative rate study of the kinetic isotope effect in the $(CH_3D) - C - 13 + Cl$ reaction, Chemical Physics Letters, 605, 152–157, 2014.

[8] Schmidt et al., 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, 17691–17696, 2013.

[9] Schmidt and Johnson, Clumped isotope perturbation in tropospheric nitrous oxide from stratospheric photolysis, Geophysical Research Letters, 42, 9, 3546–3552, 2015.

[10] Quay, P. et al.The isotopic composition of atmospheric methane, Global Biogeochemical Cycles, 13 , 2, 445–461, 1999.

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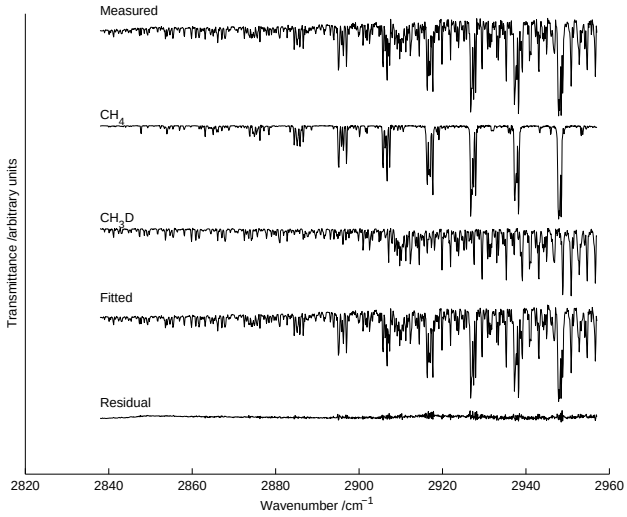

Figure 3: A typical spectral fit in the region where [$^{12}CH_4$] is obtained (Experiment 5). Experimental data are shown by the topmost line, followed by the fitted partial (synthetic) spectra of the most dominant absorbers (CH_4 and CH_3D), the resulting fitted (synthetic) spectrum (also including H_2O), and the residual between the measured and fitted spectra is shown by the bottom line.

variations, Journal of Geophysical Research: Atmospheres, 105, D11, 14531–14546, 2000.

[12] Allan et al., Active chlorine in the remote marine boundary layer: Modeling anomalous measurements of δ13C in methane, Geophysical research letters, 28, 17, 3239–3242, 2001.

[13] Allan et al., Modeling the variation of δ13C in atmospheric methane: Phase ellipses and the kinetic isotope effect, Global biogeochemical cycles, 15, 2, 467–481, 2001.

[14] Griffith, D. W. T., Synthetic Calibration and Quantitative Analysis of Gas-Phase FT-IR Spectra, Appl. Spectrosc., 50, 59–70, 1996.

[15] Griffith et al., A Fourier transform infrared trace gas analyser for atmospheric applications, Atmospheric Measurement Techniques Discussions, 5, 3, 3717–3769, 2012.

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

Table 1: Experimental setup. The experiment numbers are listed in column Exp., the detector in the column Detect., the heavy CH_4 isotopologue included in the experiments are listed in column [$^{x}CH_3D$], the mean measured temperatures in the photoreactor are listed in column T, the H_2O-vapour concentrations at the start of the experiments ($t = 0$) as obtain from spectral fitting are listed in column $[H_2O]_{t=0}$, the mean O_3 concentration after refill (i.e. the "top"-values) as obtain from spectral fitting are listed in column $[O_3]_{\mathrm{top}}$, the $^{12}CH_4$- concentrations at the start of the experiments ($t = 0$) as obtain from spectral fitting are listed in column $[^{12}CH_4]_{t=0}$, and the heavy CH_4 concentrations at the start of the experiments ($t = 0$) as obtain from spectral fitting are listed in column $[^{x}CH_3D]_{t=0}$. Note that for the experiment including CH_3D, the value of initial concentration only refers to $[^{12}CH_3D]_{t=0}$.

Exp.	Detect.	$^{x}CH_3D$	T	$[H_2O]_{t=0}$	$[O_3]_{\mathrm{top}}$	$[^{12}CH_4]_{t=0}$	$[^{x}CH_3D]_{t=0}$
			K	hPa	hPa	hPa	hPa
1	MCT	CH_3D	298.2 ± 1.2	7.1	–[a]	0.030	0.054
2	MCT	CH_3D	297.6 ± 0.8	5.6	0.19	0.058	0.042
3	MCT	CH_3D	277.2 ± 0.2	5.2	0.29	0.109	0.046
4	MCT	CH_3D	277.0 ± 0.2	5.1	0.16	0.073	0.035
5	InSb	CH_3D	284.5 ± 0.1	7.2	0.26	0.025	0.033
6	InSb	CH_3D	291.1 ± 0.2	7.4	–[a]	0.052	0.050
7	InSb	CH_3D	313.5 ± 1.3	7.1	0.17	0.025	0.029
8	InSb	CH_3D	312.4 ± 0.9	4.3	–[a]	0.022	0.040
9	InSb	$^{13}CH_3D$	298.5 ± 0.1	5.1	–[a]	0.035	0.026
10	InSb	$^{13}CH_3D$	297.6 ± 0.6	6.4	0.13	0.025	0.033
11	InSb	$^{13}CH_3D$	276.8 ± 0.8	5.4	–[a]	0.024	0.024
12	InSb	$^{13}CH_3D$	277.2 ± 1.3	5.1	–[a]	0.022	0.030
13	InSb	$^{13}CH_3D$	287.4 ± 1.2	5.4	–[a]	0.021	0.028
14	InSb	$^{13}CH_3D$	287.4 ± 0.4	4.5	–[a]	0.016	0.029
15	InSb	$^{13}CH_3D$	314.4 ± 1.0	5.2	0.26	0.023	0.037
16	InSb	$^{13}CH_3D$	313.8 ± 0.8	8.3	0.17	0.025	0.035

[a]Spectra recorded during or after photolysis, $[O_3]_{\mathrm{top}}$ not availible

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Kinetic isotope effects of $^{12}CH_3D + OH$ and $^{13}CH_3D + OH$ from 278 to 313 K

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Abstract. Methane is the second most important long lived greenhouse gas and plays a central role in the chemistry of the Earth's atmosphere. Nontheless there are significant uncertainties in its source budget. Analysis of the isotopic composition of atmospheric methane, including doubly substituted species (e.g. $^{13}CH_3D$), offers new constraints on the methane budget as the sources and sinks have distinct isotopic signatures. The most important sink of atmospheric methane is oxidation by OH in the troposphere which accounts for around $84\,\%$ of all methane removal. Here we present experimentally derived methane + OH kinetic isotope effects and their temperature dependence over the range of 278 to 313 K for CH_3D and $^{13}CH_3D$; the latter is reported here for the first time. We find $k_{CH_4}/k_{CH_3D} = 1.31 \pm 0.01$ and $k_{CH_4}/k_{^{13}CH_3D} = 1.34 \pm 0.03$ at room temperature, implying that the methane + OH kinetic isotope effect is multiplicative such that $(k_{CH_4}/k_{^{13}CH_4})(k_{CH_4}/k_{CH_3D}) = k_{CH_4}/k_{^{13}CH_3D}$, within the experimental uncertainty, given the literature value of $k_{CH_4}/k_{^{13}CH_4} = 1.0039 \pm 0.0002$. In addition, the kinetic isotope effects were characterized using transition state theory with tunneling corrections. Good agreement between the experimental, quantum chemical, and available literature values was obtained. The theoretical calculation confirms that the $^{13}CH_3D$ isotope effect is the product of D- and ^{13}C- isotope effects. Based on the results we conclude that the OH reaction (the main sink of methane) at steady-state can produce an atmospheric clumped isotope signal ($\Delta(^{13}CH_3D) = \ln([CH_4][^{13}CH_3D]/[^{13}CH_4][CH_3D])$) of 0.02 ± 0.02.

1 Introduction

Atmospheric methane is the subject of increasing interest from both the climate research community and the public due its impacts on climate change, as reported by the IPCC (2013). The direct radiative forcing of methane is 0.64 Wm^{-2}. Including feedback mechanisms and secondary effects e.g. increased O_3 production, stratospheric water vapor and production of CO_2, methane's radiative forcing becomes 0.97 Wm^{-2}, $2/3$ of the forcing by CO_2 over the same time period (IPCC, 2013, Fig. 8.15).

Atmospheric methane has both natural and anthropogenic sources and the two categories contribute about equally (Ciais et al., 2013, and references therein). Wetlands are the dominant natural source, and agriculture and waste are the largest anthropogenic sources. Fossil fuels make smaller contributions. A majority ($84\,\%$) of atmospheric methane is removed by oxidation by OH in the troposphere:

$$\mathrm{CH_4 + OH \rightarrow CH_3 + H_2O}, \tag{R1}$$

oxidation in the troposphere by Cl contributes about $4\,\%$ of the total:

$$\mathrm{CH_4 + Cl \rightarrow CH_3 + HCl}. \tag{R2}$$

About $8\,\%$ of methane is removed in the stratosphere by radical oxidation, such as reactions (R2) and (R3):

$$\mathrm{CH_4 + O(^1D) \rightarrow CH_3 + OH}. \tag{R3}$$

The rest ($4\,\%$) is removed by soil (Kirschke et al., 2013).

Carbon and hydrogen isotopic analysis are widely used to distinguish microbial and thermal sources of atmospheric methane (e.g., Lowe et al., 1997; Ferretti et al., 2005; Tyler et al., 2007; Lassey et al., 2007). However, reactions (R1), (R2), and (R3) produce relatively large D/H isotope effects (Saueressig et al., 1995, 1996, 2001; Crowley et al., 1999; Feilberg et al., 2005). Thus, the construction of an accurate top-down methane budget by isotopic analysis, must take the isotopic signatures of both sources and sinks into account (Quay et al., 1999; Bergamaschi et al., 2000; Allan et al., 2001a, b) [new references]. An isotope budget based on methane source (and sink) fractionations result in an underdetermined systems (e.g., Pohlman et al., 2009). 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. $[^{12}\mathrm{CH_4}][^{13}\mathrm{CH_3D}] = [^{13}\mathrm{CH_4}][^{12}\mathrm{CH_3D}]$). 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 kinetic isotope effect ${}^{j}E\alpha$ is a characteristic property of each process:

$$ {}^{j}E\alpha \equiv \frac{k({}^{i}E + OH)}{k({}^{j}E + OH)}, \tag{1} $$

where ${}^{i}E$ is the most abundant (here, the lighter) isotopologue, ${}^{j}E$ the rare (heavy) isotopologue, $k(E + OH)$ is the reaction rate coefficient for the reaction $E + OH$. As a measure of how much of a fractionation of $^{13}CH_3D$ kinetic reactions produce, the apparent clumpiness, γ is used. It is a measure of the effect of the clumped substitution on the reaction rate, as opposed to the combined effect of two single substitutions. It is defined as (Wang et al., 2015):

$$ \gamma \equiv \frac{{}^{13C,D}\alpha}{{}^{13C}\alpha \times {}^{D}\alpha} \tag{2} $$

A related measure is the $\Delta(^{13}CH_3D)$ value that quantifies the extent to which rare isotopes clump together to form a multiply substituted species, as opposed to a stochastic distribution (Ono et al., 2014):

$$ \Delta(^{13}CH_3D) \equiv \ln\left(\frac{[^{13}CH_3D][^{12}CH_4]}{[^{12}CH_3D][^{13}CH_4]}\right), \tag{3} $$

where $[^{13}CH_3D]$, $[^{12}CH_4]$, $[^{12}CH_3D]$ and $[^{13}CH_4]$ represent the concentrations of the different isotopologues.

The kinetic isotope effects for the singly substituted species CH_3D and $^{13}CH_4$ have been studied previously both experimentally and theoretically, see Tables 3 and 4 [table reordered] respectively. The kinetic isotope effect ${}^{13C,D}\alpha$ for the reaction with OH is not described in the existing literature. The related kinetic isotope effect for the $CH_4 + Cl$ reaction was measured at room temperature with the present setup by Joelsson et al. (2014) and found to be 1.60 ± 0.04.

In the present study the kinetic isotope effects ${}^{D}\alpha$ and ${}^{13C,D}\alpha$ are determined using the relative rate method. Species concentrations in the reaction cell are determined using Fourier Transform Infrared (FTIR) spectroscopy. Further, ${}^{D}\alpha$, ${}^{13C}\alpha$, and ${}^{13C,D}\alpha$ are calculated using quantum chemistry and transition state theory.

2 Experimental procedures

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 ($T = [298, 278, 288, 313]\mathrm{K} = [25, 5, 15, 40]^{\circ}\mathrm{C}$); two experiments were conducted for each temperature.

2.1 Relative rate method

The experiments were carried out using the relative rate method on a semi-static gas mixture. The decaying concentrations of reactants were measured as a function of the extent of reaction. Considering two bimolecular reactions with second order rate coefficients k_{A} and k_{B},

$$\mathrm{A} + \mathrm{OH} \xrightarrow{k_{\mathrm{A}}} \mathrm{Products}, \tag{R4}$$

$$\mathrm{B} + \mathrm{OH} \xrightarrow{k_{\mathrm{B}}} \mathrm{Products}, \tag{R5}$$

and assuming there were no other loss processes, the following relation holds:

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}\right) = \frac{k_{\mathrm{A}}}{k_{\mathrm{B}}} \ln\left(\frac{[\mathrm{B}]_0}{[\mathrm{B}]_t}\right). \tag{4}$$

Here $[\mathrm{A}]_0$, $[\mathrm{A}]_t$, $[\mathrm{B}]_0$ and $[\mathrm{B}]_t$ represent the concentrations of compounds A and B at times 0 and t respectively. The slope of $\ln([\mathrm{A}]_0/[\mathrm{A}]_t)$ versus $\ln([\mathrm{B}]_0/[\mathrm{B}]_t)$ gives the relative reaction rate coefficient. In these experiments A is $^{12}CH_4$ and B is $^{12}CH_3D$ or $^{13}CH_3D$.

2.2 Photoreactor

Experiments were carried out in the photochemical reactor at the University of Copenhagen, Department of Chemistry. The reactor has been described in detail elsewhere (Nilsson et al., 2009). It consists of a 100 L quartz cell with multi-pass optics surrounded by 16 UV-C fluorescent Hg lamps in a temperature controlled housing. The cell is coupled to a Bruker IFS 66v/S FTIR spectrometer with either a mercury cadmium telluride (MCT) detector (Experiments 1–4) or an indium antimonide (InSb) (Experiments 5–16). The InSb-detector has a better signal-to-noise ratio, the MCT-detector is used in Experiments 1–4 for logistical reasons. Two thermocouple gauges are placed inside the temperature controlled housing to monitor the temperature and a pressure gauge is connected to the cell to monitor pressure inside the cell. The temperatures and the pressures were logged every 0.5 s.

2.3 Laboratory proceedure

Gas mixes were prepared by expanding H_2O vapor (Milli-Q Ultrapure Water) into the chamber through a glass gas manifold. The two methane isotopologues CH_3D (Experiments 1–8) (purity $> 98\%$, Cambridge Isotope Laboratories, Inc.) or $^{13}CH_3D$ (Experiments 9–16), and CH_4 (purity $> 99\%$, Aldrich) and O_3 were flushed into the chamber with a N_2 buffer (purity 99.998%, Air Liquide), all at the concentrations given in Table 1 [table reordered]. $^{13}CH_3D$ was synthesized using the

Grignard reaction, see Joelsson et al. (2014). O_3 was generated from O_2 (purity 99.97 %, Air Liquide) using an ozone generator (Model AC-20, O_3 Technology), preconcentrated before injection on silica gel cooled with ethanol and dry ice to $-67°C$. The desired pressure in the cell (450 hPa) was obtained using N_2 as bath gas. The starting pressure is chosen such that the pressure is high enough for the N_2 to quench $O(^1D)$ radicals, but low enough to keep the final pressure below atmospheric pressure. The gas mixture was left to rest for up to 1.5 $hours$ while several IR spectra were recorded to ensure that no instability or dark chemistry occurs in the gas mix. The UV-C lamps were lit for up to 5 min photolysing at least 75 % of the O_3 according to:

$$O_3 + h\nu \rightarrow O(^1D) + O_2. \quad \text{(R6)}$$

$O(^1D)$ then subsequently reacts with H_2O to yield OH:

$$O(^1D) + H_2O \rightarrow OH + OH. \quad \text{(R7)}$$

Up to 0.2 Pa O_3 was flushed with about 20 hPa N_2 into the chamber to compensate for the loss of ozone with time, mainly due to $O(^3P) + O_3$. A pressure gradient was established and maintained throughout the filling process such that no gas leaked back from the chamber into the gasline. Spectra were recorded at each filling step. The procedure was repeated until the mix had a final pressure of 933 hPa. Two experiments were conducted at each of the temperatures 278, 288, 298, and 313 K for each of the two heavy methane istopologues. Exact temperatures are listed in Table 1 [new table]. After each experiment a dilution test was performed: 133 hPa was pumped out and the chamber is refilled with 133 hPa N_2. This was repeated 5–6 times. Ideally, concentration calculations from the spectral fits (data analysis described below) of the resulting spectra should give a linear fit with the slope of 1. The slope of these dilution tests are presented in Table 2 [new table]. In an extra experiment with $^{12}CH_3D$, N_2O (Air Liquide, no purity information available) was added as an $O(^1D)$ tracer. The results from this experiment are used as a benchmark to validate a model that was constructed to investigate the extent of $O(^1D)$ chemsitry, see Sect. 2.5. An example of an experimental plot can be found in Fig. 4 [new figure] and the full data set in Figs. S1–S8 in the Supplement.

2.4 Data analysis

The experimental IR spectra were analyzed using the program MALT which simulates experimental FTIR spectra (Griffith, 1996) combined with non-linear least squares fitting to best-fit the calculated spectra to measured spectra (Griffith et al., 2012) [new reference]. The MALT program generates a simulated spectrum from initial estimates of the absorber concentrations and instrument parameters. The residual between the experimental and simulated spectra is reduced through iteration. Simulated line-shapes are generated using HITRAN absorption parameters (version 2008) (Rothman et al., 2009) convolved with an FTIR instrument function simulating the Bruker IFS 66v/S instrument. The $InSb$ detector covers a spectral range from 1800–5000 cm^{-1} and the MCT detector covers a

Table 1. Experimental setup. The experiment numbers are listed in column Exp., the detector in the column Detect., the heavy CH_4 isotopologue included in the experiments are listed in column $[^{x}CH_3D]$, the mean measured temperatures in the photoreactor are listed in column T, the H_2O-vapour concentrations at the start of the experiments ($t = 0$) as obtain from spectral fitting are listed in column $[H_2O]_{t=0}$, the mean O_3 concentration after refill (i.e. the "top"-values) as obtain from spectral fitting are listed in column $[O_3]_{top}$, the $^{12}CH_4$- concentrations at the start of the experiments ($t = 0$) as obtain from spectral fitting are listed in column $[^{12}CH_4]_{t=0}$, and the heavy CH_4 concentrations at the start of the experiments ($t = 0$) as obtain from spectral fitting are listed in column $[^{x}CH_3D]_{t=0}$. Note that for the experiment including CH_3D, the value of initial concentration only refers to $[^{12}CH_3D]_{t=0}$.

Exp.	Detect.	$^{x}CH_3D$	T /K	$[H_2O]_{t=0}$ /hPa	$[O_3]_{top}$ /hPa	$[^{12}CH_4]_{t=0}$ /hPa	$[^{x}CH_3D]_{t=0}$ /hPa
1	MCT	CH_3D	298.2 ± 1.2	7.1	–[a]	0.030	0.054
2	MCT	CH_3D	297.6 ± 0.8	5.6	0.19	0.058	0.042
3	MCT	CH_3D	277.2 ± 0.2	5.2	0.29	0.109	0.046
4	MCT	CH_3D	277.0 ± 0.2	5.1	0.16	0.073	0.035
5	InSb	CH_3D	284.5 ± 0.1	7.2	0.26	0.025	0.033
6	InSb	CH_3D	291.1 ± 0.2	7.4	–[a]	0.052	0.050
7	InSb	CH_3D	313.5 ± 1.3	7.1	0.17	0.025	0.029
8	InSb	CH_3D	312.4 ± 0.9	4.3	–[a]	0.022	0.040
9	InSb	$^{13}CH_3D$	298.5 ± 0.1	5.1	–[a]	0.035	0.026
10	InSb	$^{13}CH_3D$	297.6 ± 0.6	6.4	0.13	0.025	0.033
11	InSb	$^{13}CH_3D$	276.8 ± 0.8	5.4	–[a]	0.024	0.024
12	InSb	$^{13}CH_3D$	277.2 ± 1.3	5.1	–[a]	0.022	0.030
13	InSb	$^{13}CH_3D$	287.4 ± 1.2	5.4	–[a]	0.021	0.028
14	InSb	$^{13}CH_3D$	287.4 ± 0.4	4.5	–[a]	0.016	0.029
15	InSb	$^{13}CH_3D$	314.4 ± 1.0	5.2	0.26	0.023	0.037
16	InSb	$^{13}CH_3D$	313.8 ± 0.8	8.3	0.17	0.025	0.035

[a] Spectra recorded during or after photolysis, $[O_3]_{top}$ not availible

spectral range from 400–5000 cm^{-1}. 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 [new figures]. 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

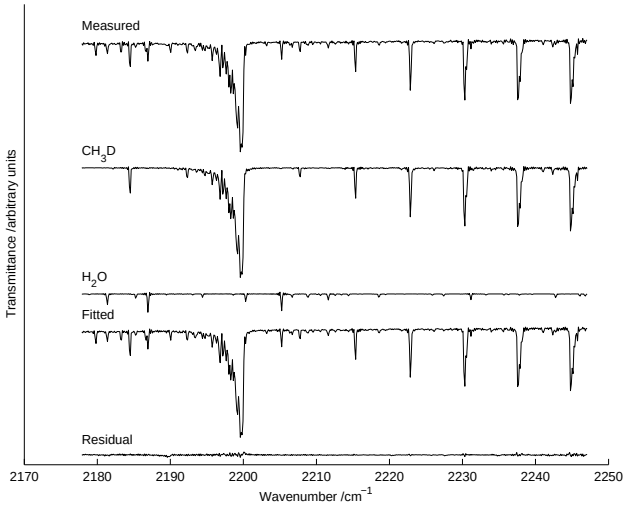

Figure 1. A typical spectral fit in the region where [$^{12}CH_3D$] is obtained (Experiment 5). Experimental data are shown by the topmost line, followed by the fitted (synthetic) partial spectra of the most dominant absorbers (CH_3D and H_2O), the resulting fitted (synthetic) spectrum (also including CO_2 and CO), and the residual between the measured and fitted spectra is shown by the bottom line.

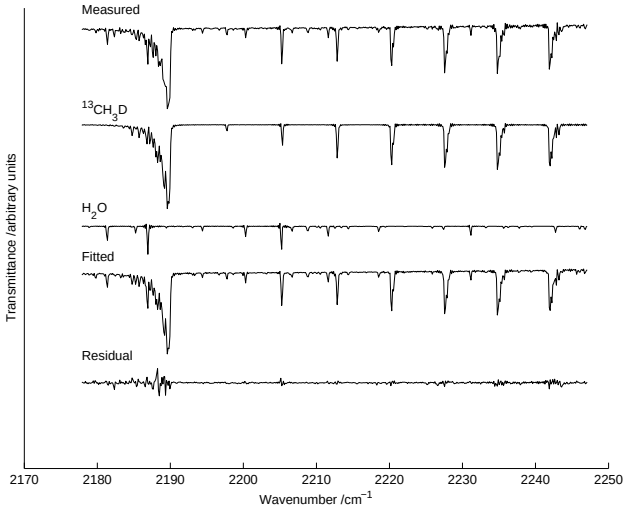

Figure 2. A typical spectral fit in the region where [$^{13}CH_3D$] is obtained (Experiment 10). Experimental data are shown by the topmost line, followed by the fitted (synthetic) partial spectra of the most dominant absorbers ($^{13}CH_3D$ and H_2O), the resulting fitted (synthetic) spectrum (also including CO_2 and CO), and the residual between the measured and fitted spectra is shown by the bottom line.

simulated spectra obtained from the HITRAN database in the fit, see Fig. 3 [new figure]. The spectral windows were sometimes adjusted to exclude saturated lines.

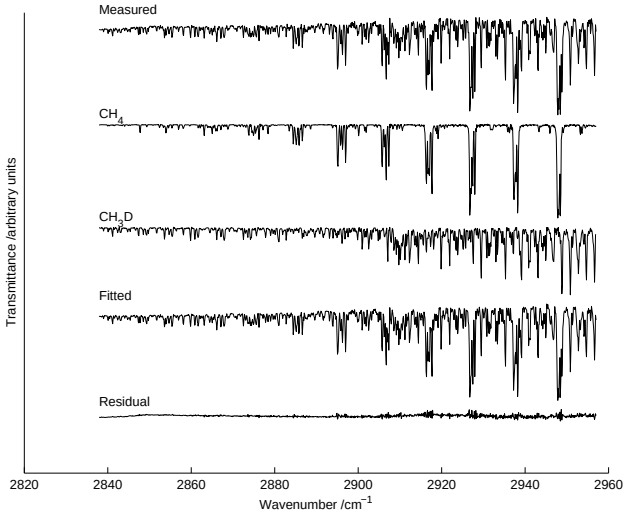

Figure 3. A typical spectral fit in the region where $[^{12}CH_4]$ is obtained (Experiment 5). Experimental data are shown by the topmost line, followed by the fitted partial (synthetic) spectra of the most dominant absorbers (CH_4 and CH_3D), the resulting fitted (synthetic) spectrum (also including H_2O), and the residual between the measured and fitted spectra is shown by the bottom line.

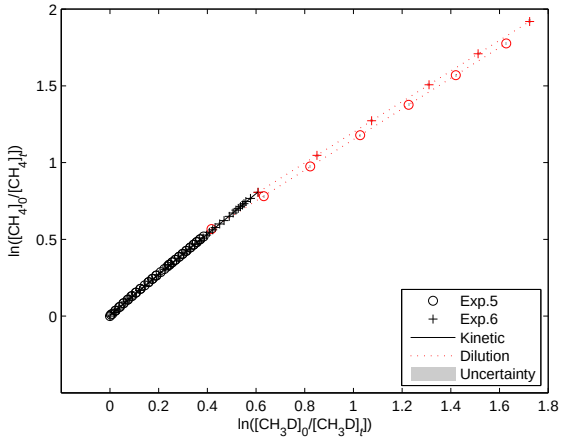

Figure 4. A typical experimental outcome, Experiment 5 and 6: CH_3D, $T = 288$K. Experimental data are shown using black open circles (Exp. 5) and black plus signs (Exp. 6). Corresponding dilution test points are shown using red symbols. A linear fit of the experimental points is shown using a black solid line and linear fit of the subsequent dilution test are represented by a red dotted line, uncertainties for each point are represented by gray areas.

After $[^{x}CH_3D]$ (where $x = 12$ or $x = 13$) and $[^{12}CH_4]$ were obtained from the spectral analysis, $\ln([^{x}CH_3D]_0/[^{x}CH_3D]_t)$ was plotted against $\ln([^{12}CH_4]_0/[^{12}CH_4]_t)$ as described in Sect. 2.1. A straight line was fitted to these data points using a weighted total least squares routine (York et al.,

2004). The fitting procedure takes uncertainties in both dimensions into account. The uncertainty $\sigma\left(\ln\left([\mathrm{A}]_0/[\mathrm{A}]_t\right)\right)$ was calculated using standard error propagation:

$$\sigma\left(\ln\left([\mathrm{A}]_0/[\mathrm{A}]_t\right)\right) = \sqrt{\left(\frac{\sigma([\mathrm{A}]_0)}{[\mathrm{A}]_0}\right)^2 + \left(\frac{\sigma([\mathrm{A}]_t)}{[\mathrm{A}]_t}\right)^2} \tag{5}$$

where $\sigma([\mathrm{A}]$ was obtained as output from MALT. The fitting proceedure, performed using a MATLAB script (York et al., 2004), also yields an error estimation which is defined as the uncertainty of the kinetic isotope effect $\sigma(\alpha)$. An example of a straight line fit can be found in Fig. 4 [new figure] and the full data set in Figs. S1–S8 in the Supplement. In the temperature dependence curve fitting procedure, the parameters A and B are from a linearized version of the Arrhenius equation:

$$\ln(k) = \ln(A) + B \cdot T^{-1} \tag{6}$$

are adjusted to match experimental. Also here, the method of York et al. (2004) was used. 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.

2.5 Kinetic model

A kinetic model was used to determine the influence of $\mathrm{O}(^1\mathrm{D})$, reaction (R3), which rivals Reaction (R1).The model is previously described and was used by Nilsson et al. (2012). However, only the methane reaction subset and associated ($\mathrm{O_x}$ and $\mathrm{HO_x}$) chemistry were used here. The Kintecus program (Ianni, 2003), simulates the photolysis of $\mathrm{O_3}$ and the following oxidation chain of $\mathrm{CH_4}$.[sentence removed] To model ozone photolysis accurately, the modeled $\mathrm{O_3}$ was matched to the measured value by adjusting the photolysis rate, then the model was verified by comparing the decrease of $\mathrm{CH_4}$ and the increase of $\mathrm{H_2O}$ during the experiment. The model was run for each refill of $\mathrm{O_3}$, where the reaction rates of Reactions (R1) and (R3) were obtained. The model was designed for room temperature; experiments at other temperatures were not modeled. Experiment 2 was thus modeled: 4.4% of $\mathrm{CH_4}$ was estimated to be lost to Reaction (R3). In an additional experiment $\mathrm{N_2O}$ was introduced in the chamber as an $\mathrm{O}(^1\mathrm{D})$-tracer. Since $\mathrm{N_2O}$ does not react with OH and is not photolyzed at the wavelengths present (Nilsson et al., 2009), the decreased of $\mathrm{N_2O}$ should be only due to Reaction (R8):

$$\mathrm{N_2O} + \mathrm{O}(^1\mathrm{D}) \rightarrow \text{products.} \tag{R8}$$

The amount of $\mathrm{CH_4}$ lost by reaction (R3) can therefore be approximated by:

$$1 - \frac{[\mathrm{CH_4}]_t}{[\mathrm{CH_4}]_0} = 1 - \exp\left(-k_{(\mathrm{R3})}[\mathrm{O}(^1\mathrm{D})]t\right) = 1 - \frac{[\mathrm{N_2O}]_t}{[\mathrm{N_2O}]_0}^{\left(k_{(\mathrm{R8})}/k_{(\mathrm{R3})}\right)}, \tag{7}$$

where $k_{(R8)} = 1.27 \times 10^{-10} \mathrm{cm}^{-3}\mathrm{s}^{-1}$ and $k_{(R3)} = 1.75 \times 10^{-10} \mathrm{cm}^{-3}\mathrm{s}^{-1}$ (Sander et al., 2010). This gives 2.3% $[CH_4]$ lost by oxidation of $O(^1D)$, Reaction (R3). The kinetic model described above estimated that 4.7 % $[CH_4]$ were lost by Reaction (R3) for this additional experiment. Both methods agree that $O(^1D)$ loss is a minor channel. No correction is applied, and the possible deviation is included in the estimated error.

3 Theoretical procedure

Rate constants and kinetic isotope effects for $CH_4 + OH$ were calculated using a procedure similar to that employed by Joelsson et al. (2014).

3.1 Computational chemistry calculations

The geometries of reactants, products and transition states were determined using a geometry optimization procedure based on the unrestricted MP2 method (Møller and Plesset, 1934) and the aug-cc-pVQZ orbital basis set (Dunning Jr., 1989; Woon and Dunning Jr., 1993). Harmonic vibrational frequencies for all relevant isotopologues of reactants, products, and transition states were obtained at the same level of theory. The calculations were carried out using the Gaussian 09 program package (Frisch et al., 2009).

The electronic energy of the optimized structures were refined using the CCSD(T) method (Watts et al., 1993; Knowles et al., 1993, 2000) with aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z basis sets. The results from the different basis sets were used to extrapolate the electronic energy at the complete basis set limit following the approach of Halkier et al. (1998) as described by Joelsson et al. (2014).

3.2 Rate constant calculations

The abstraction of a CH_4 hydrogen atom by OH can occur at four different sites. Depending on the methane isotopologue in question, these sites are either distinguishable or indistinguishable. Microscopic rate constants are calculated for hydrogen abstraction at each site using classical transition state theory with a tunneling correction factor,

$$k^{(i)}_{\mathrm{micro}} = \eta^{(i)}_{\mathrm{tun}} \frac{k_b T}{h} \frac{Q^{(i)}_{\mathrm{TS}}}{Q_{\mathrm{reac}}} \exp\left(-\Delta E^{(i)}/RT\right) \tag{8}$$

where $\Delta E^{(i)}$ is the reaction barrier height (including the zero point vibrational energy) for the i'th reaction path. $\eta^{(i)}_{\mathrm{tun}}$ is a tunneling correction factor obtained using the Wigner tunneling correction (Wigner, 1932). $Q^{(i)}_{\mathrm{TS}}$ and Q_{reac} are the partition functions for the transition state and reacting pair, respectively. The total rate constant is obtained by summing over the microscopic rate constants.

Table 2. Results. The experiment numbers are listed in column Exp., the heavy CH_4 isotopologue included in the experiments are listed in column $^{x}CH_3D$, the mean measured temperatures in the photoreactor are listed in column T, the kinetic isotope effect corresponding to the isotopologue are listed in column α, and the result of the dilution experiments are listed in column k_{dil}.

Exp.	$^{x}CH_3D$	T/K	α	k_{dil}
1	CH_3D	298.2 ± 1.2	1.302 ± 0.038	1.011 ± 0.048
2	CH_3D	297.6 ± 0.8	1.314 ± 0.020	–[a]
3	CH_3D	277.2 ± 0.2	1.294 ± 0.017	0.962 ± 0.037
4	CH_3D	277.0 ± 0.2	1.335 ± 0.017	–[a]
5	CH_3D	284.5 ± 0.1	1.334 ± 0.012	0.999 ± 0.009
6	CH_3D	291.1 ± 0.2	1.323 ± 0.010	0.998 ± 0.010
7	CH_3D	313.5 ± 1.3	1.301 ± 0.007	1.006 ± 0.031
8	CH_3D	312.4 ± 0.9	1.338 ± 0.010	–[a]
9	$^{13}CH_3D$	298.5 ± 0.1	1.359 ± 0.022	1.000 ± 0.029
10	$^{13}CH_3D$	297.6 ± 0.6	1.314 ± 0.007	0.990 ± 0.064
11	$^{13}CH_3D$	276.8 ± 0.8	1.357 ± 0.046	1.016 ± 0.031
12	$^{13}CH_3D$	277.2 ± 1.3	1.344 ± 0.013	1.008 ± 0.030
13	$^{13}CH_3D$	287.4 ± 1.2	1.346 ± 0.025	1.009 ± 0.022
14	$^{13}CH_3D$	287.4 ± 0.4	1.342 ± 0.015	1.011 ± 0.019
15	$^{13}CH_3D$	314.4 ± 1.0	1.316 ± 0.016	1.003 ± 0.038
16	$^{13}CH_3D$	313.8 ± 0.8	1.331 ± 0.033	1.001 ± 0.034

[a] No dilution test performed

4 Results and Discussion

The results of the 16 individual experiments (eight for each isotopologue) are tabulated in Table 2 [new table]. The resulting $^{D}\alpha$, $^{13C}\alpha$, and $^{13C,D}\alpha$ values from the experimental and theoretical studies are tabulated in Tables 3, 4, and 5 [tables reordered] along with previous experimental and theoretical results. The results are also shown in Fig. 5 and 6 for reactions of CH_3D and $^{13}CH_3D$ respectively.

The exponential curve fits yielded the parameters presented in Tables 3 and 5 giving $^{D}\alpha_{\text{Arr}} = 1.32 \pm 0.13$ and $^{13C,D}\alpha_{\text{Arr}} = 1.32 \pm 0.20$ at $T = 298\text{K}$. The mean of results of room temperature experiments Experiments 1 and 2, and Experiments 9 and 10 is $^{D}\alpha_{\text{exp}} = 1.31 \pm 0.01$ and $^{13C,D}\alpha_{\text{exp}} = 1.34 \pm 0.03$ [uncertainty corrected] respectively. It follows that $\gamma_{\text{exp}} = 1.02 \pm 0.02$ at $T = 298\text{K}$, using $^{13C}\alpha_{\text{exp}} = 1.0039 \pm 0.0002$ (Saueressig et al., 2001), meaning that the clumped isotope might react slower relative to what would be predicted based on the kinetic isotope effects of CH_3D and $^{13}CH_4$. However, if the Arrhenius parameters are used to calculate the kinetic isotope effects at

Table 3. Experimental and theoretical studies of ${}^{\mathrm{D}}\alpha$. The temperature dependence studies are presented in the Arrhenius form ${}^{\mathrm{D}}\alpha(T) = A(T/298\mathrm{K})^n \exp(BT^{-1})$, where A, n, and B are tabulated, T is the given temperature range, and ${}^{\mathrm{D}}\alpha(T = 298\mathrm{K})$ is the resulting kinetic isotope effect at $T = 298\mathrm{K}$. Where no B coefficient is presented A can be taken as ${}^{\mathrm{D}}\alpha(T)$ for the given temperature range. All uncertainties are given as one standard deviation (σ).

Study	A	n	B/K	T/K	${}^{\mathrm{D}}\alpha(T = 298\mathrm{K})$
Experimental studies					
Present study[a]	1.23 ± 0.08	0	21 ± 21	[278,313]	1.31 ± 0.01[h]
Saueressig et al. (2001)[b]	1.294 ± 0.009	–	–	296	–
Gierczak et al. (1997)[c]	1.09 ± 0.05	0	49 ± 11	[220,415]	1.25 ± 0.07
DeMore (1993)[a]	0.91	0	75	[298,360]	1.17
Gordon and Mulac (1975)[d]	1.50	–	–	416	–
Gordon and Mulac (1975)[d,i]	1.06	–	–	416	–
Theoretical studies					
Present study[e]	1.314	0	6.354	[200,300]	1.339
Sellevåg et al. (2006)[f]	[1.30, 1.00]	–	–	[200,1500]	1.27
Masgrau et al. (2001)[g,j]	1.00	-0.02	50.5	[200,1500]	1.25

[a] Fourier transform infrared spectroscopy - relative rate
[b] Tunable diode laser absorption spectroscopy - isotope ratio mass sectrometer
[c] Pulsed photolysis - pulsed laser-induced flourescence
[d] Pulse radiolysis
[e] Transition state theory with Wigner tunneling correction
[f] Canonical unified statistical theory
[g] Multicoefficient correlation method
[h] Average room temperature value, not obatined from curve fit
[i] Re-evaluated by DeMore (1993)
[j] Arrhenius parameters available at (NIST, 2015)

$T = 298\mathrm{K}$, $\gamma_{\mathrm{Arr}} = 1.00 \pm 0.18$ (i.e. the reaction has no clumping effect). All uncertainties are given as one standard deviation (σ). The theoretical results gives $\gamma_{\mathrm{theory}} = 1.00$ at $T = 298\mathrm{K}$.

The present experimental room temperature results for ${}^{\mathrm{D}}\alpha$ agree, to within the error bars, with the previous experimental studies, with the exception of DeMore (1993). DeMore (1993) used FTIR spectroscopy with a slow flow setup where the two methane isotopologues were measured seperately with a common reference compound. The low ${}^{\mathrm{D}}\alpha$ value in DeMore (1993) may be explained by interference from $\mathrm{O}(^1\mathrm{D})$ radicals: OH radicals were produced by photolysis of $\mathrm{O_3}$ at 254 nm in the presence of $\mathrm{H_2O}$, as in the present study. A relatively high rate of reaction (R3) would reduce the final kinetic isotope effect, since the kinetic isotope effect for oxidation with $\mathrm{O}(^1\mathrm{D})$ is smaller than the kinetic isotope effect for the oxidation of OH (Saueressig et al., 2001). The present experimental results of ${}^{\mathrm{D}}\alpha$ are also in good agreement with Masgrau et al. (2001) and Sellevåg et al. (2006). The

Table 4. Experimental and theoretical studies of ${}^{13\mathrm{C}}\alpha$. The temperature dependence studies are presented in the Arrhenius form ${}^{13\mathrm{C}}\alpha(T) = A\exp(BT^{-1})$, where A and B are tabulated, T is the given temperature range, and ${}^{13\mathrm{C}}\alpha(T = 298\mathrm{K})$ is the resulting kinetic isotope effect at $T = 298\mathrm{K}$. Where no B coefficient is presented A can be taken as ${}^{13\mathrm{C}}\alpha(T)$ for the given temperature range. All uncertainties are given as one standard deviation (σ).

Study	A	B/K	T/K	${}^{\mathrm{D}}\alpha(T = 298\mathrm{K})$
Experimental studies				
Saueressig et al. (2001)[a]	1.0039 ± 0.0002	–	296	–
Cantrell et al. (1990)[b]	1.0054 ± 0.0005	–	[273, 353]	1.0054 ± 0.0005
Rust and Stevens (1980)[c,i]	1.003	–	–	–
Theoretical studies				
Present study[d]	1.0137	-1.219	[200,300]	1.0094
Sellevåg et al. (2006)[e]	$[1.014, 1.00]$	–	[200,1500]	1.003
Gupta et al. (1997)[f]	1.010	–	300	–
Melissas and Truhlar (1993)[gh]	$[1.005, 1.001]$	–	[223,416]	1.005
Lasaga and Gibbs (1991)[h]	[1.0036,1.0076]	–	[150,350]	–

[a] Tunable diode laser absorption spectroscopy - isotope ratio mass sectrometer

[b] Gas chromatography - mass spectrometry

[c] Isotope ratio mass spectrometry

[d] Transition state theory with Wigner tunneling correction

[e] Canonical variational transition state theory

[f] Conventional transition state theory

[g] Interpolated variational transition state theory with centrifugal-dominant, small-curvature tunneling coefficients

[h] Ab initio calculations

[i] No temperature information available

Table 5. Experimental and theoretical studies of ${}^{13\mathrm{C,D}}\alpha$. The temperature dependencies are presented in the Arrhenius form ${}^{13\mathrm{C,D}}\alpha(T) = A\exp(BT^{-1})$, where A and B are tabulated, T is the given temperature range, and ${}^{13\mathrm{C,D}}\alpha(T = 298\mathrm{K})$ is the resulting kinetic isotope effect at $T = 298\mathrm{K}$. All uncertainties are given as one standard deviation (σ).

Study	A	B/K	T/K	${}^{\mathrm{D}}\alpha(T = 298\mathrm{K})$
Experimental study[a]	1.18 ± 0.10	38 ± 26	[278,313]	1.34 ± 0.03[c]
Theoretical study[b]	1.328	5.301	[200,300]	1.349

[a] Fourier transform infrared spectroscopy - relative rate

[b] Transition state theory with Wigner tunneling correction

[c] Average room temperature value, not obatined from curve fit

theoretical calculations of ${}^{\mathrm{D}}\alpha$ give a slightly higher value than the experimental results, although they are in good agreement with the best Arrhenius curve fit at $T = 298\mathrm{K}$.

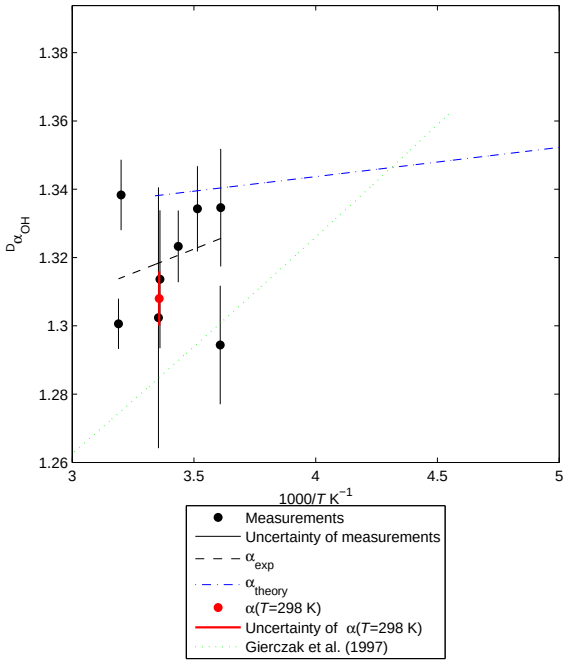

Figure 5. The individual measurements of ${}^{\mathrm{D}}\alpha$, are represented by black points; the accompaning individual error bars are represented by thin black solid lines; the experimental Arrhenius curve fit is represented by a black dashed line; the theoretical Arrhenius curve fit is represented by a blue dashed-dotted line; the mean of the room temperature measurements are represented by a red solid circle; the uncertainty of the room temperature measurements are represented by a thick red solid line; the result from Gierczak et al. (1997) (which is included for comparison) are represented by a green dotted line. All uncertainties are given as one standard deviation (σ).

The experimental room temperature result for ${}^{13\mathrm{C,D}}\alpha = 1.34 \pm 0.03$ agrees to within the error bar with both the theoretical value and the best estimate of the Arrhenius curve fit at $T = 298\mathrm{K}$.

The theoretical calculations show a very small temperature dependence; the variability in the experimental data is large compared to the value of the slope, making a quantification of the temperature dependence uncertain. Furthermore, the theoretical analysis revealed that the primary cause for the kinetic isotope effect is the substantially reduced reactivity of the D atom, which, in turn, can be explained by a significant increase in reaction barrier due to changes in vibrational zero point energy and to a lesser extent tunneling.

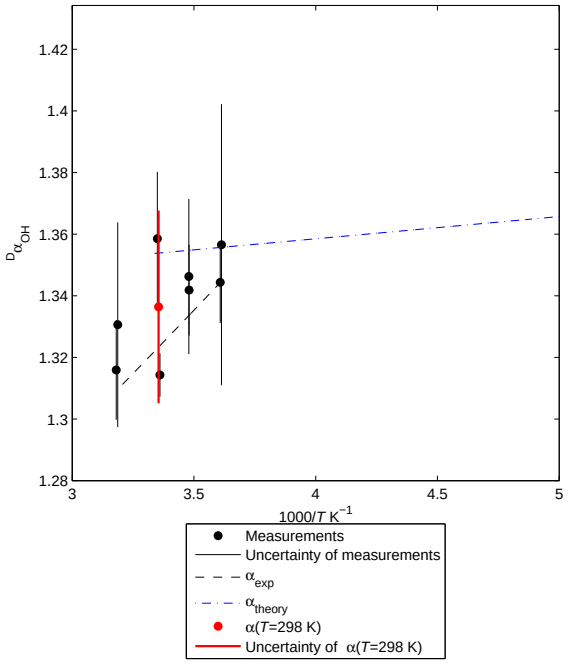

Figure 6. The individual measurements of ${}^{13\mathrm{C,D}}\alpha$, are represented by black points; the accompaning individual error bars are represented by thin black solid lines; the experimental Arrhenius curve fit is represented by a black dashed line; the theoretical Arrhenius curve fit is represented by a blue dashed-dotted line; the mean of the room temperature measurements are represented by a red solid circle; the uncertainty of the room temperature measurements are represented by a thick red solid line. All uncertainties are given as one standard deviation (σ).

4.1 Atmospheric implications

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

5 Conclusions

We present experimentally derived $CH_4 + OH$ kinetic isotope effects and their temperature dependence for CH_3D and $^{13}CH_3D$; the latter is reported for the first time. We find $^{D}\alpha = 1.31 \pm 0.01$ and $^{13C,D}\alpha = 1.34 \pm 0.03$ at room temperature, implying that the kinetic isotope effect is multiplicative such that $(k_{CH_4}/k_{^{13}CH_4})(k_{CH_4}/k_{CH_3D}) = k_{CH_4}/k_{^{13}CH_3D}$ [new expression] to within the experimental uncertainty. We compare our experimental results to theoretical estimates derived using transition state theory with tunneling correction and kinetic isotope effects reported in the literature. We find good agreement between theoretical and literature values. Based on these experiments we find that the OH reaction (the main sink of methane) at steady-state has a clumped $\Delta(^{13}CH_3D) = 0.02 \pm 0.02$.

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