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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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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.

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Interactive Discussion
Discussion Paper

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 (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. $[^{12}CH_4][^{13}CH_3D] = [^{13}CH_4][^{12}CH_3D]$). However, small deviations from stochastic distribution can be induced by ther-

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modynamic (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: "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; Allan et al. 2001b)."

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

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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 tracking methane sources than conventional isotopic analysis. However, the present uncertainty overrides the current estimated methane source signals (), 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

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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 1-3 (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 (Griffith 1996) combined with non-linear least squares fitting to best-fit the calculated spectra to measured spectra (Griffith et al. 2012)."

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

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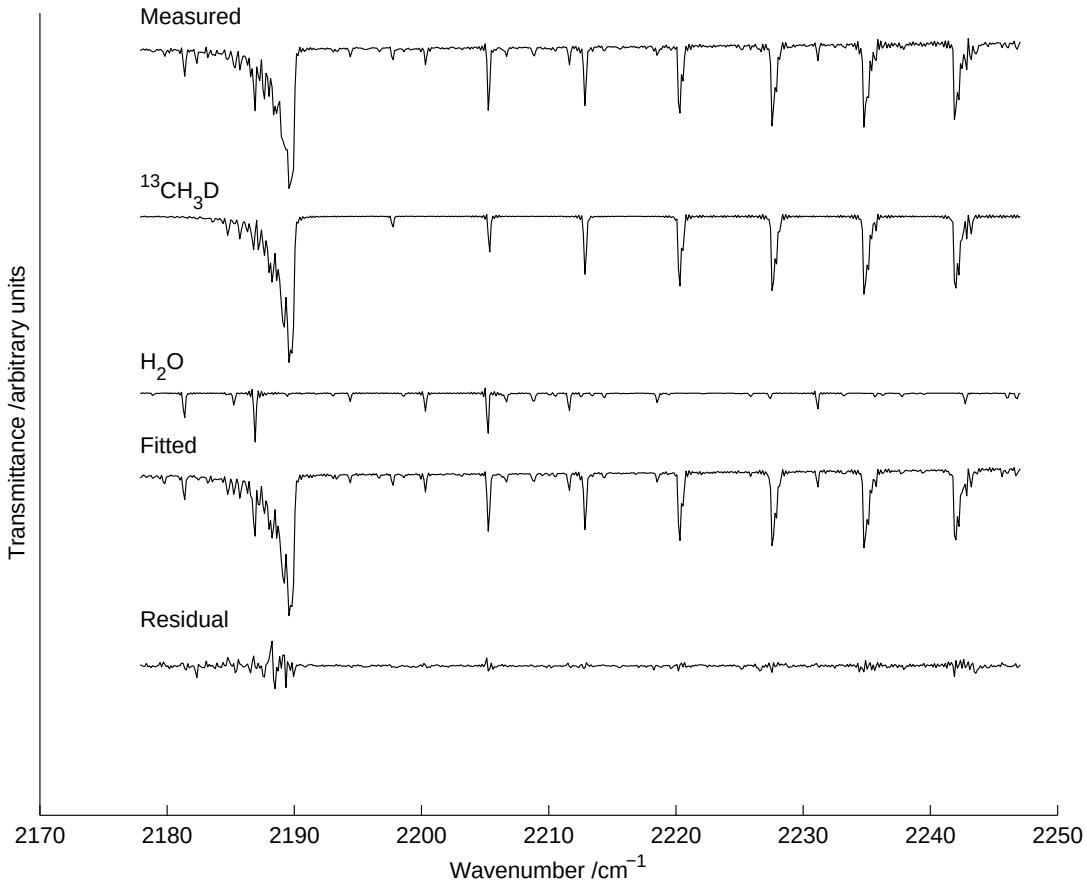

Fig. 1.

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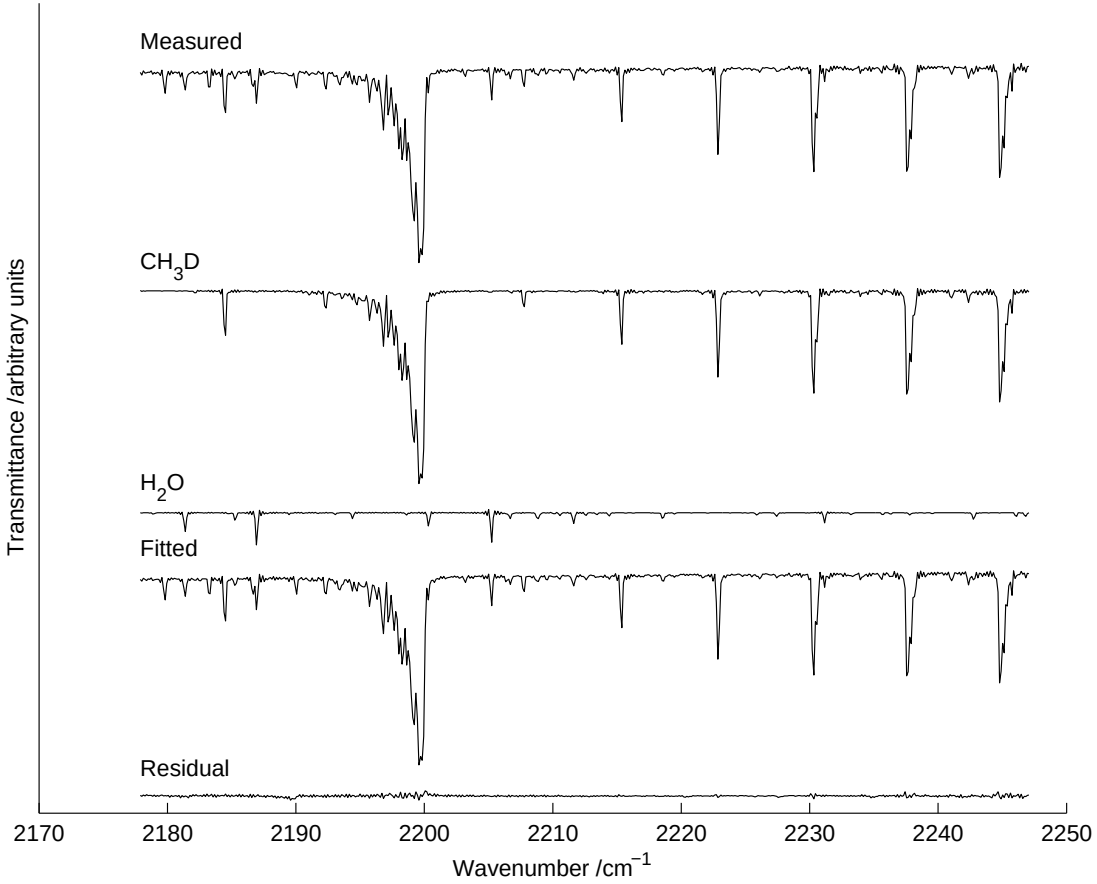

Fig. 2.

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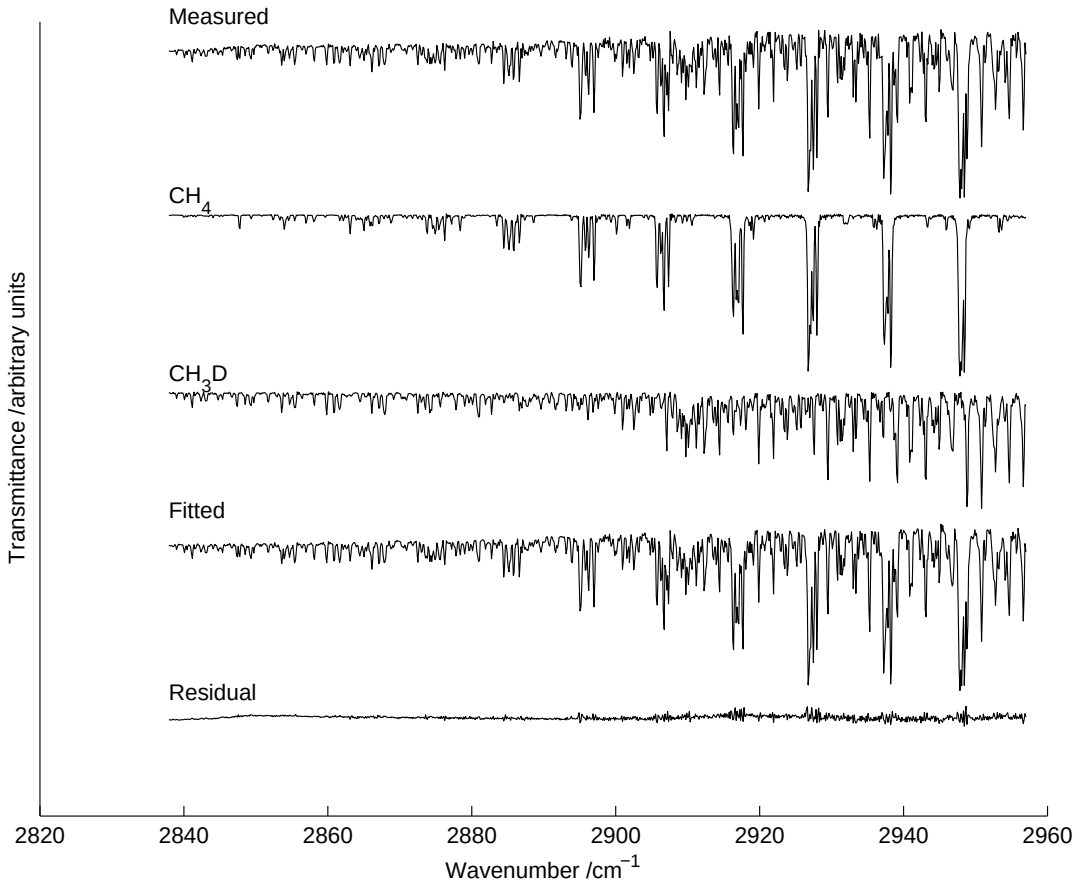

Fig. 3.

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