Atmos. Chem. Phys. Discuss., 15, C9224–C9227, 2015
www.atmos-chem-phys-discuss.net/15/C9224/2015/


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.

**Anonymous Referee #1**

Received and published: 12 November 2015

This study investigated of isotope effect on CH4 + OH system. In particular, authors for the first time tried to investigate isotope effect on 13CH3D, clumped isotopes of CH4. Using relative rate method, determination of relative rate coefficients for CH3D and 13CH3D relative to 12CH4 were measured. The OH radicals are produced from O3 photolysis and reaction with O1D and H2O in the chamber, and authors tried to determined temperature dependence of isotope effects. They also confirmed possible systematic error on FTIR measurements using dilution experiments. In addition to the experiments, authors did theoretical calculations. Thus, the series of experiments sound scientifically, and the presented results are interesting and certainly new. However, I think this is too compact, and discussions of experimental results are not enough. Although this study is interesting and clumped CH4 is potentially new tool



Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

for atmospheric chemistry and physics, I do not think this manuscript is not enough for publication because of lack of explanation of experimental results and analyses. In addition, no description for interpretation (and implication) of the data for atmospheric chemistry and physics are discussed in the manuscript. I, therefore, think this manuscript need major revision and I recommend authors to add several sections as suggested following.

Major comments

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". 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? What is the difference (and advantage) from conventional isotopic information of CH4? (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.

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



ACPD
15, C9224–C9227, 2015

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.

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 recommended.

Minor comments: L14: (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.

Finally, I am not English speaker, I apologize the very poor English writing.



ACPD
15, C9224–C9227, 2015

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 27853, 2015.



ACPD

15, C9224–C9227, 2015