

### Point-by-point response to the issues raised by referee#3

We thank the referee for the helpful comments and suggestions which have improved the manuscript.

#### Referee #3 (*referee's comments are in italics*)

*The paper presents isotope fractionation measurements of CH<sub>3</sub>Cl for the reactions with hydroxyl and chlorine radicals and CH<sub>4</sub>+OH. This is a valuable contribution to the hitherto scarce information on hydrogen kinetic isotope effect of reactions significant for the atmosphere. Isotopes deliver valuable adjunct information which can, together with other data, increase the understanding of the atmospheric processes. Therefore the paper is highly suitable to be published in the journal. The paper contains yet some weak points which need to be improved before publishing.*

Authors: We very much thank the referee for the positive evaluation of our manuscript. The comments of the referee are addressed below

#### *Major comment*

*The major issue which should be made clearer to the reader is linked to the necessity of very accurate concentration and isotopic composition of the reactant during its degradation for delivering reliable epsilon values. Since during both oxidation reactions of CH<sub>4</sub> and CH<sub>3</sub>Cl a similar temporal evolution of the concentration is observed, it should exist one order of magnitude difference in the produced OH concentration. For the former, this should be in the range of 10<sup>10</sup> cm<sup>-3</sup> range, which is very ambitious for the photooxidation of ozone method. The authors should give some more details about designing the experiments, for instance on ozone concentration, UV lamp intensity...To rule out any losses of the very small methane molecule (wall permeation, tightness), it would be helpful to add a figure (also as supplement) depicting a 'zero-run', i.e. the concentration evolution of methane in the FEP bag without reaction during the time of 10 h.*

Authors: The reviewer is correct with his estimate of the OH concentration. In our study, OH was generated by UV-photolysis of ozone in the presence of water vapour. This is a well-established efficient method for OH radical generation (DeMore 1992, Cantrell et al. 1990). In order to perform the degradation experiments within a day, the experimental conditions were modified for the different experiments as indicated by the new Table S1 which has been added to the supplementary information file of the revised manuscript. Based on the high radiant efficiency of the TUV lamp at the absorption band of O<sub>3</sub> the photolysis of O<sub>3</sub> to O<sup>1</sup>D and O<sub>2</sub> and the subsequent OH generation by O<sup>1</sup>D+H<sub>2</sub>O is favoured. One can estimate a photolysis rate of J(O<sub>3</sub>) in the range of 10<sup>-3</sup> s<sup>-1</sup> for the first experiment with CH<sub>3</sub>Cl. For the CH<sub>4</sub> experiments we even had 4 TUV lamps installed around the chamber, which increased the J(O<sub>3</sub>) value. This is represented by the reduced lifetime of O<sub>3</sub> when the lamps are on and no O<sub>3</sub> is injected (roughly 11 min for the CH<sub>3</sub>Cl+OH experiment and 4 min for the CH<sub>4</sub>+OH experiment). The reaction rate of OH for CH<sub>3</sub>Cl is roughly 6 times higher than for CH<sub>4</sub> (based on the higher O<sub>3</sub> concentrations 623 ppbv over 9h for CH<sub>3</sub>Cl+OH and 3570 ppbv over 13h for CH<sub>4</sub>+OH. These differences have been specified in the revised manuscript and related data has been provided in the Supplementary (Table S1). Furthermore, we have added data and a related discussion section to the Supplementary that rule out any unaccounted loss of methane during our experiments.

Finally, please note that we also have added a third degradation experiment of CH<sub>3</sub>Cl+OH to the manuscript. These data have only recently become available and were included in the revised manuscript to improve statistical considerations. Thus the mean isotope fractionation for the reaction of CH<sub>3</sub>Cl+OH has slightly changed from -242 to -263‰.

*Other comments*

*Page2Line62: The authors might consider to add a short statement on the significance of CH<sub>3</sub>Cl losses into the stratosphere.*

Authors: Added as requested.

*Page3Lines83-84: reformulate, the authors give themselves enough literature sources*

Authors: Change applied.

*Page8Equation2: The authors should revise the consistency of this equation: they should keep 1000 also behind the second '='. This is dependent on the delta expression, and as it looks like (behind the first '='), this is in  $\times 10^{-3}$ , permil, or the unusual murey.*

Authors: Change applied. Furthermore, we have replaced mUr by ‰ throughout the whole manuscript.

*Editorial revisions:*

*Page6Line 141: replace PFA by PFH*

Authors: Change applied.