

Interactive comment on “NO_x cycle and tropospheric ozone isotope anomaly: an experimental investigation” by G. Michalski et al.

Anonymous Referee #2

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Journal: ACP Title: NO_x cycle and tropospheric ozone isotope anomaly: an experimental investigation Author(s): G. Michalski et al. MS No.: acp-2013-32 MS Type: Research Article

The authors present a laboratory study of NO_x chemistry and try to extrapolate for atmospheric application. The laboratory result itself is of interest. However the validity of the extrapolation is not verified. Though it may be valid, the authors have to demonstrate. Therefore, I cannot recommend publication at the present form.

Major comments:

1. The statements/descriptions in some places are not accurate. I'll point out below (may not be complete), but the authors should be more careful/serious of the presentation.

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tation.

2. Lab has O₃/NO₂ much lower than the ambient. Extrapolation may or may not work. As authors said in the ms that it's not possible to do the experiment at a condition similar to the ambient. The authors should at least do modeling and understand the key processes that affect NO₂/O₃. If the governing reactions for low O₃/NO₂ ratio condition (lab.) are the same as those for real condition (ambient), their experimental results may be applicable. The model should be constructed to reproduce NO_x diurnal cycle to some extent.

Other comments:

1. Abstract: The authors mentioned that NO_x isotopic equilibrium can be reached in hours to days/weeks. Can the equilibrium be reached in the real atmosphere? Can steady state value be reached? Also it seems to me that steady state value quoted here simply represents the isotope value of ozone. If this is the case, say that explicitly.
2. Introduction first sentence: to be more precise, a key driver of pollution chemistry
3. Page 9446 last sentence of the 1st paragraph: “but most fall below” need to be more explicit. Now the statement stands there with no point.
4. Same page middle of the bottom paragraph: “in view of the large number of possible reactions,” one has to identify key reactions that affect the isotopic composition of the species of interest. Key reactions that affect the isotopologue distribution may not be the same as key reactions for control the abundance. The authors should be more clearly on this.
5. Page 9448 top paragraph: is the assumption valid? One can make it more quantitative, based on the modeling results.
6. Page 9449, line 5: how high is high? Need to be more quantitative.
7. Same paragraph: 1 h steady state time needs to be justified. Again can be obtained

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from their models and do longer exposure.

8. Section 2.2: the authors shift back and forth between total quantify and mixing ratio, which make the article difficult to follow. Mixing ratio is more relevant, and I'd suggest change all to vmr and put the amount in bracket.

9. Section 3: should be Fig. 4

10. the following sentence: where is 20 ppmv from? I can't see it from the figure.

11. Same page bottom paragraph: "hypothesis." The authors need to use model with the existing reactions to justify the statement of NO oxidation and NO_x-O₂ isotope exchange.

12. Page 9451 1st paragraph: the description can be more quantitative, using the modeling results. Whether a reaction is important depends crucially on the partitioning of its reaction rate

13. Page 9456 1st paragraph: collisional fractionation is considered for the reaction Q + ONO. For consistency, the same should be applied to others. However in the last sentence of the paragraph, it is said to ignore any kinetic isotope effect. Please clarify this and explain why not consider.

14. Same page near the end of 2nd paragraph: The fitted rate coefficient is 0.004 s⁻¹. Is the value consistent with the dissociative flux you put in? What is (or are) key reaction that affects the NO₂ isotopic composition? How well is the rate coefficient determined?

15. Same sentence: what channel symmetry factor? Please be more explicit. What reactions in the table do the authors refer to?

16. Next sentence: The current paper deals with oxygen isotopes. N has no (or little) effect on oxygen. Why nitrogen isotope is mentioned here? Unless N can interfere O.

17. Page 9457 bottom paragraph: ambient [O₃]/[NO] is not much less than 1, which is

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very different from the current experimental condition. One has to discuss/present in detail the key reactions and check similarity and/or difference between the 2 conditions.

18. Page 9458 1st paragraph: how long is NO quenching time (lifetime) when light is off?

19. Page 9459 the last few sentences of the top paragraph: I could not follow the descriptions from "Additionally, they refer to the photolytically ... applications." If O+O₂ isotope exchange is a lot faster than O₃ or NO₂ dissociation rate, then O would have little (or negligible) memory to whether it's from O₃ or NO₂. The authors should be aware of this. Presenting modeling results will help to clarify this. Also what limitation do the authors refer to? It's too vague. Moreover model can be used to tell whether the current lab results are appropriate for atmospheric application.

20. Page 9462 1st paragraph: I can't follow the statement that peroxy can affect final D₁₇O but not equilibration time. This is true if NO oxidation by HO₂ is a process much slower than O₃ oxidation. If that's the case, D₁₇O would not be affected by HO₂.

21. Conclusion: validation of the extrapolation needs to be presented. Please also be explicit about the O₃ isotopic composition in the troposphere (near the surface). It seems to me that steady state isotope values should reflect the isotopic composition of O₃ (more specifically asymmetric O₃).

22. Fig 1: why isotope values increase first and then decrease, at 35 min. How do you justify that 1-hour is sufficient to reach equilibration/steady state.

23. Redundant figures: The authors should present more model results to validate their extrapolation. For example, Fig 5c is basically the same as Fig 5a. Also Fig 6 and Fig 7.

24. Fig 2, Fig 3: instead of NO₂ amount or O₂ pressure, NO₂/O₂ ratio may be better.