

Interactive comment on “Investigation of potential interferences in the detection of atmospheric RO_x radicals by laser-induced fluorescence under dark conditions” by H. Fuchs et al.

Anonymous Referee #3

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Review of Fuchs et al.: "Investigation of potential interferences in the detection of atmospheric RO_x radicals by laser-induced fluorescence under dark conditions"

The manuscript describes results of experiments studying dark processes potentially causing OH artifact signals in the LIF instruments developed by Juelich group, using a flow reactor and a large chamber. Tested processes included O₃ + olefin reactions (with OH scavenger), NO₃ injection, and laser photolysis of acetone. At the concentration levels relevant to the real atmosphere, these processes did not produce significant artifact. On the other hand, at significantly increased concentrations of the reactants, the O₃ + olefin reactions gave measurable OH artifact. A working hypothesis was that

C4839

stabilized Criegee intermediates were involved in the formation process of OH in the inlet zone. The obtained results, including insensitivity against SO₂ injection, did not readily support this hypothesis. NO₃ injection was found to produce internal OH for the first time, but only with high NO₃ concentrations. The mechanism that NO₃ reactions produced OH was not specified. The possibility of heterogeneous reactions or involvement of molecular clusters, depending on the cell design, was suggested. The nighttime ambient OH concentrations observed in China up to 10⁶ cm⁻³ remained unexplained by these tested dark reactions, suggesting that real atmospheric processes unidentified yet should be responsible. Although it is still difficult to specify processes giving different degrees of artifact across several OH detection cells designed by different groups, characterization of each detection cell is important and informative. The logic is sound, and the topic is suitable for the journal. However, there are several points requiring more explanations, as listed below. The reviewer recommends publication after adequate response to the issues.

1. page 12477, line 24. In this paragraph past observations on nighttime OH concentrations are discussed. The observed ambient OH concentration levels that the authors consider should be figured out around here, for easier reading. In the current manuscript, information on the observed nighttime concentration levels only appeared at the end of the manuscript (page 12501).
2. page 12478, line 2. Nighttime NO concentrations shown by Lu et al. (2014) were sometimes very high, after O₃ was titrated.
3. page 12482, line 8. How about the beam temperature for the two detection cells?
4. page 12486, Section 3. Is it possible to theoretically calculate OH concentrations produced from acetone photolysis, if the absorption cross section, OH yield, and the laser fluence are known?
5. page 12489, line 5. Internal OH may not be produced on the laser axis and thus the artifact signal may behave differently against propane addition from the case of O₃

C4840

photolysis test. Several tests were made with propane mixing ratio up to 800 ppmv. Is this mixing ratio still low enough not to deplete the internal OH if present?

6. page 12489, line 20 and Table 1. What does "n/a" mean in Table 1? For the high alkene concentration cases, OH signal without propane was below detection limit? With propane addition, the OH signal started to increase? If so, some more explanation needs to be given, as internal formation of OH from intermediate species from O₃ + olefin reactions must have occurred even in the case without propane. Some reasons need to be present to explain why the signal was not seen when propane was not added.

7. page 12492, line 23. Do the authors discuss loss of "internally produced" OH here? If loss of OH introduced from the nozzle is discussed, the factor of diffusion loss must have been taken into account by calibration performed at different pressure conditions.

8. page 12494, lines 3-5. I do not understand why a different topic of heterogeneous wall loss or reactions in molecular clusters is discussed in this paragraph. As in the both paragraphs above and below a possibility of OH artifact produced from longer-lived product from ozonolysis reactions is discussed, this possibility should be mentioned later.

9. page 12500, line 2. Do the authors assume that OH is directly produced from the NO₃ + VOC reactions for the calculation of possible OH concentration?

10. page 12501, line 8. Halocarbon wax coating of the external and internal surfaces of the nozzle may help evaluating the influence from heterogeneous processes.

11. page 12502, line 3. Which day (2nd day?) of HOxComp experiment do the authors examine here?

12. Table 1. Steady-state concentrations of OH expected for individual experiments should be listed.

13. Figure 1. The design of "cell purge" in the used two instruments might be important
C4841

and should be discussed.

14. Figure 5, caption. What do the authors mean by "ambient conditions"?

15. Figure 7. What is LIF corr? Is this the signal level after subtraction of O₃ interference? How does the OH artifact levels in Figure 7 compare with those plotted in Figure 5, in terms of the turnover rate?

16. Figure 8. The used two colors for the two series are difficult to distinguish.

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