

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.

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We thank the reviewer for the helpful comments.

Comment: 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).

Response: We will add on p12477 l26: “During our field campaigns in China 2006,

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nighttime OH concentrations reached values up to $3 \times 10^6 \text{ cm}^{-3}$."

Comment: page 12478, line 2. Nighttime NO concentrations shown by Lu et al. (2014) were sometimes very high, after O₃ was titrated.

Response: We will add on p12478 l4: "However, NO can also accumulate during nighttime, when all ozone has already been titrated."

Comment: page 12482, line 8. How about the beam temperature for the two detection cells?

Response: The sampled air is cooled down in the inlet nozzle due to adiabatic gas expansion. Further downstream, however, the air flow warms up again and reaches room temperature in the detection volume of both OH cells as indicated by the rotational distribution in the OH excitation spectrums in both detection cells.

Comment: page 12486, Section3. 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?

Response: The magnitude of the OH concentration produced by laser photolysis of acetone can be estimated from the concentration of photolytically formed acetyl radicals. Using the absorption cross-section ($\sigma = 1.6 \times 10^{-20} \text{ cm}^2$ at 308 nm, 25°C, IUPAC data sheet P7) of acetone, the pressure-dependent quantum yield for CH₃CO ($\Phi_{R1} = 0.63$ at 308 nm, 25°C, 4 hPa, Carr et al., Chem. Phys. Lett., 2007) and an assumed laser power of 10 mW (308 nm, pulse repetition rate of 8.5 kHz), an acetyl radical concentration of about 9 cm^{-3} is produced per laser pulse from 5 ppbv of acetone at 4 hPa (cell pressure) in the laser beam. Reaction R2 is sufficiently fast to convert almost all acetyl to OH within the residence time (ca. 0.13 ms) of the sampled-air flow which crosses the path of the laser beam. Accordingly, the estimated OH concentration produced per laser pulse from acetone is about 10 cm^{-3} in the detection cell at the given conditions. From the measured interference ($0.05 \times 10^6 \text{ cm}^{-3}$ at 1 atm), an

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order of magnitude larger value of 200 cm^{-3} is calculated for the same conditions. This larger value can be explained, if part of the sampled air (containing acetone) mixes with slower flowing sheath-gas adjacent to the fast gas flow, still being in the viewing zone of the PMT. An effective residence time of the slower flowing gas in the laser beam in the order of a few ms would be sufficient to explain the OH signal from acetone photolysis.

Comment: 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 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?

Response: We thank the reviewer for this important comment. 800 ppmv of propane would still be acceptable in the short-inlet cell, but the experiments with propene and ethene were performed in the long-inlet cell where the residence time is long enough to deplete internal OH significantly by 800 ppmv of propane. We have therefore repeated the measurement with 100 ppmv of propane for which we calculate a reduction of internal OH by no more than 30%. We found that ozonolysis of propene at similar turnover rates as we used for monoterpenes give similar results, but results for ethene gave similar results as before. We will add these result to Fig. 5, change Table 1 accordingly and change the text:

p12491 l28: We will cancel the statement about propene.

p12489: "Further experiments were conducted at much higher concentrations of ethene (with mixing ratios up to 12 ppmv, propene (with mixing ratios up to 1.7 ppmv) and limonene, α -pinene (both with mixing ratios up to 70 ppbv), and isoprene (mixing ratios up to 450 ppbv) and ozone mixing ratios of up to 900 ppbv (Table 1) using the cell with the long inlet. Sufficient propane was always added to scavenge externally produced OH during these experiments.

Significant internal OH production is observed in the case of high propene α -pinene, limonene and isoprene concentrations (Table 1). In the case of ethene no significant

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signal was observed.”

p12495: “In the case of ethene, the Criegee intermediate CH_2OO is formed, which is not expected to efficiently produce OH (Johnson et al. 2008).

In the case of propene the stabilized Criegee CH_3CHOO is formed for which (Novelli et al. 2014) showed that CH_3CHOO can decompose in the inlet of an LIF instrument for OH detection. In that work, the reaction of 500 ppbv ozone with 70 ppmv propene gave apparent OH concentrations of up to $1 \times 10^8 \text{ cm}^{-3}$ in the presence of propane as OH scavenger. The authors also show that the efficiency of the detection has a maximum at a few milliseconds after the air has entered the detection cell. Scaling results at this high turnover rate of the ozonolysis reaction to the turnover rates used in our experiments gives lower OH concentrations than observed in our experiments. However, no exact agreement is expected because internal OH was partly scavenged by the high propene concentration used in Novelli et al. 2014.”

We will cancel the statement on p12503 l28/29.

Comment: 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 O_3 + 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.

Response: In these experiments OH production in the absence of propane was not quantified. In some of these experiments, the reaction of OH with the high alkene concentration competed with the reaction of propane, so that the measurement without propane does not give additional information. An OH signal was observed in the absence of propane which was partly due to the internal OH production and OH produced in the flow tube. We will indicate this more precisely in the revised version of the

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manuscript.

Comment: 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.

Response: We are discussing potential loss of internally produced OH at the surfaces inside the fluorescence cell. Loss in the nozzle is taken into account by the calibration and affects only OH that is sampled from outside the fluorescence cell.

Comment: 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.

Response: We will move this paragraph to p12496 l11.

Comment: page 12500, line 2. Do the authors assume that OH is directly produced from the $\text{NO}_3 + \text{VOC}$ reactions for the calculation of possible OH concentration?

Response: This estimate only demonstrates that any hypothetical gas-phase mechanism that is initiated by $\text{NO}_3 + \text{VOC}$ and yields OH is not sufficient to explain the observations. Even direct OH production from a reaction at the gas-kinetic collision rate would not be fast enough. We do not imply that such a reaction exists, but any other potential mechanism would have an even lower OH production rate.

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

Response: We thank the reviewer for this suggestion. We are certainly working on this topic to further minimize this interference.

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

Response: This statement does not refer to a particular experiment of the HOxCOMP campaign. The differences in the HO₂ measurements in the dark were largest on the second day, but occurred also in the other experiments.

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

Response: A similar question was raised by reviewer 2 and we would like to refer to our answer there.

Comment: Figure 1. The design of “cell purge” in the used two instruments might be important and should be discussed.

Response: We will add on p12481 l8: “The longer residence time of air in the fluorescence cell with the long inlet presumably results in a better mixing of ambient air and the nitrogen purge flow compared to the cell with the short inlet.”. Experiments do not indicate that the two cells behave differently except for the longer residence time of air. Therefore, we do not think that a further discussion of this issue is required.

Comment: Figure 5, caption. What do the authors mean by “ambient conditions”?

Response: We mean room temperature and normal pressure. We will change the caption accordingly.

Comment: 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?

Response: A similar question was raised by reviewer 1. We would like to refer to our response there.

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

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Response: We will changes colors in this figure.

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 12475, 2015.

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