

Interactive comment on “Intercomparison of peroxy radical measurements obtained at atmospheric conditions by laser-induced fluorescence and electron spin resonance spectroscopy” by H. Fuchs et al.

H. Fuchs et al.

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We thank the referee for his/her review and useful comments. Listed below are our responses to the comments and changes made to the revised manuscript.

Comment As calibration of the instruments is key it would be useful to extend the description of the calibration procedures for ROxLIF in this manuscript, and to enlarge on the method by which the MIESR sensitivity is determined (in addition to the references available elsewhere). In particular the instrument accuracy, precision and detection limits should be quoted as distinct quantities, for each system, under both chamber and ambient conditions (radical levels; see below).

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Response In our opinion, the calibration procedure of ROxLIF is described with sufficient detail for the purpose of this report on pp. 382 and 383 and readers are referred to our recent publication which describes the calibration in more detail. The instrument accuracy and precision are quoted on p. 383. We extended this by adding: "The estimated accuracy of calibration is approximately 20 % (2σ) limiting the accuracy of ROxLIF measurements. If sampling highly polluted air, interferences such as thermal decomposition of atmospheric peroxy nitrates could reduce the accuracy, but such conditions were not encountered in the current experiments.". Details are discussed in Fuchs et al., Rev. Sci. Instr., 79, 084104, 2008. The MIESR technique is an absolute measurement, which does not require a calibration of its sensitivity, as pointed out on p. 384. We thank the referee for noticing that MIESR accuracy is not mentioned. We added on p 384: "The accuracy of measurements is 5 %".

Comment I would question if the instruments have been compared under truly atmospheric conditions as the radical levels in the experiments (30-40 ppt for both HO₂ and RO₂) are rather higher than those found in much of the atmospheric boundary layer, which will also contain many other species which may contribute to or affect the measured signal. Will the instrument performance be equivalent under typical real atmospheric boundary layer conditions? Will other atmospheric constituents e.g. varying levels of humidity affect the LIF measurement?

Response The referee is right that maximum concentrations of peroxy radicals reached during these experiments, are at the high end of atmospheric levels. Maximum concentrations found in the atmosphere are typically 30-40 pptv (e.g. Cantrell et al., J. Geophys. Res. 108, 8797, 2003 and Mihelcic et al., J. Geophys. Res. 108, 8254, 2003), but can be as high 80 pptv (A. Hofzumahaus, EOS Trans. AGU, 89(53), Fall Meet. Suppl., Abstract A13F-06). The purpose of these experiments was to check the calibration of the the new ROxLIF instrument for HO₂, CH₃O₂ and C₂H₅O₂ with an independent instrument, MIESR. Concentrations of radicals were within the range of atmospheric concentrations but experiments were carried out without the complication

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of unknown components contained in ambient air to be able to identify potential problems. There are some small, known interferences for the LIF detection as mentioned above and discussed in Fuchs et al., Rev. Sci. Instr., 79, 084104, 2008. Water vapor only affects the yield of fluorescence photons, because of well-known quenching of the OH fluorescence, which can be corrected (Fuchs et al., Rev. Sci. Instr., 79, 084104, 2008), but there is no chemical interference as observed for the radical amplification in PERCA instruments. We added on p. 383: "The sensitivity of the instrument is corrected for fluorescence quenching by water vapor, but there is no chemical interference from water vapor as observed in PERCA instruments (Mihele and Hastie, 1998)."

Comment Radical speciation: While the methane experiment will contain only CH₃O₂ and HO₂, the 1-butene system contained C₂H₅O₂ and CH₃O₂, please give the precise response factors to the different RO₂ radicals. Is the ROxLIF performance in this regard similar to that previously observed for PERCA (e.g. Ashborn et al., J Atmos Chem 29, 233, 1998)? In the ozonolysis system, does the instrument respond to the stabilised Criegee species, C₂H₅CHOO and CH₂OO, which may be present?

Response Here, only CH₃O₂ and HO₂ radicals were generated for calibration of ROxLIF measurements. As stated on p. 382, the instrument's sensitivity has been carefully characterized earlier for different types of RO₂ radicals and was found to be essentially the same for CH₂O₂ and C₂H₅O₂ as expected from reaction kinetics (Fuchs et al., Rev. Sci. Instr., 79, 084104, 2008). This result is different from observation for the PERCA instrument described by Ashborn et al. However, chemical and physical conditions in the RO₂ conversion reactor such as pressure, geometry and surface material are different between this instrument and the PERCA. As mentioned in the response to comments of Referee 1, stabilized Criegee species are expected to decompose in the reaction with high CO present in the ROxLIF conversion reactor to no-radical products, which cannot be detected by ROxLIF.

Comment To what extent was the intercomparison conducted in a blind manner, as in the recent HOxCOMP campaign?

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Response In contrast to measurements during the HOxCOMP campaign, this inter-comparison was not carried out in a formal blind manner. We added on p. 384 to clarify the procedure: "Raw data were evaluated independently by different operators of the two instruments without communicating results before final data were exchanged."

Comment A key aspect of the LIF HO₂ detection is that there is insufficient time (or [O₂]) for RO₂ to be converted to OH by reaction with the added NO within the LIF system low pressure region; this point should be made in the ROxLIF description.

Response We thank the referee for this suggestion and added on p. 382: "In contrast to previous detection of HO₂ by LIF, where RO₂ conversion was limited by the short reaction time and dilution of oxygen required in reaction R12, the reaction time of 0.6 s is long enough and the oxygen concentration high enough for quantitative conversion."

Comment The instrument sampling heights are somewhat different, which should be unimportant in a well-mixed chamber, but the MIESR sampling height at 2 cm is rather close to the chamber floor. You mention minimising possible instrument surface losses for the ROxLIF system; are there any data regarding effects of wall proximity on radical levels in such chambers or with this system?

Response Most likely radicals are lost on surfaces of the chamber, but losses are hard to quantify from these experiments. However, we are confident that there are no radial concentration gradients, which would influence this intercomparison (see response to Referee 1).

Comment The large methane mixing ratio present in the chamber will compete with CO for reaction with OH in the ROxLIF reduced pressure RO₂ conversion section; I calculate that ca. 10% of the OH will react with CH₄ rather than CO at the levels given (CO, 0.17%; CH₄, 0.5%). Will this affect the ROxLIF measurements?

Response The referee is correct that the high methane concentration has an effect on the sensitivity of the ROxLIF measurement because of the competition between

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OH+CO and OH+CH₄ reaction. We added a paragraph at the end of section 4.1: "The high methane concentration in the chamber led to a reduction in the ROxLIF sensitivity, because OH radicals produced in the conversion reactor partly regenerated CH₃O₂ radicals. Model calculations of the reaction kinetics in the reactor show a reduction of the sensitivity of 4% for RO₂ 9% and for HO₂ for a methane mixing ratio of 0.5%. Since methane was not measured during this experiment and the initial mixing ratio was only estimated from its addition before the experiment started, this effect was not taken into account in the data evaluation and adds to the uncertainty in the ROxLIF measurements."

Comment In the conclusions section, the retirement of the Jülich MIESR system is discussed. While this may be a development of interest to the community, a research journal manuscript is possibly not the vehicle for communication of such institutional decisions.

Response We canceled the statement.

Comment p.377 Only certain VOCs are oxidised by NO₃.

Response We are aware of this fact and changed the text to: "many atmospheric hydrocarbons" (line 1)

Comment Define NO_x.

p.377 Line 8; The NO_x steady state does not affect O₃ *once steady state is achieved*, but the initial titration of O₃ by reaction with exhaust-derived NO does lead to changes in NO/NO₂/O₃; need to clarify the statement

p.378 10 ppt is a typical daytime *maximum* level

p.378 line 12 *at* the time of calibration

p.380 line 13 arranged in a cylindrical shape

p.391 line 7 allowed the design of

Response We thank the referee for these suggestions and edited the text accordingly.

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Comment p.382 line 13 Strictly you cannot achieve complete chemical conversion, rather the HO₂ undergoes an exponential decay

Response We changed the text to "nearly complete" to be more precise.

Comment p.388 Strictly the RO₂ levels are not *entirely* controlled by the O₃ / alkene levels as they undergo self- and cross-reactions also (plus HO₂+O₃).

Response We canceled "entirely" to be more precise.

Interactive comment on Atmos. Meas. Tech. Discuss., 1, 375, 2008.

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1, S164–S169, 2009

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