

## ***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.***

### **Anonymous Referee #2**

Received and published: 18 December 2008

This paper describes a comparison between measurements of hydro- and organic-peroxy radicals performed by a new instrument, ROxLIF, and the established MIESR technique, within the simulation chamber SAPHIR. The essence of the ROxLIF technique is to convert peroxy radicals to HO<sub>2</sub> in a reduced-pressure pre-reactor, the HO<sub>2</sub> is then detected as OH (through titration with added NO) by laser-induced fluorescence; the technique therefore extends the scope of the established LIF method for OH and HO<sub>2</sub> to include RO<sub>2</sub> species. The paper presents data from one experiment in which methyl peroxy radicals generated from methane photo-oxidation were measured

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simultaneously in SAPHIR by MIESR and ROxLIF, and data from further experiments in which the ozonolysis of 1-butene was used to generate HO<sub>2</sub> and RO<sub>2</sub>, with measurements performed by ROxLIF and MIESR during separate experiments one week apart, but performed under identical conditions. The two measurement methods are in impressive agreement for both HO<sub>2</sub> and RO<sub>2</sub> in each case, which certainly gives some confidence that both systems are performing well (or at least similarly). It was unfortunate that the second experiment was not a simultaneous intercomparison but the data shown indicate that the two experiments were pretty similar, and the authors have quantified the (small) difference between the runs.

The subject of the paper is appropriate for AMT, and presents new scientific findings which are of importance in validating the performance of the new instrument. I recommend publication if the following comments can be addressed:

Some of the reasons for performing measurement intercomparisons such as the one described here are to identify unforeseen interferences or problems with the measurement methods, to assess the accuracy of calibration approaches, and more widely to inform the community of the accuracy and precision which might be anticipated from radical measurements in the real atmosphere. I would encourage the authors to expand their discussion to address the following points :

-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).

-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 HO<sub>2</sub> and RO<sub>2</sub>) are rather higher than those found in much of the atmospheric boundary layer, which will

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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 ?

-Radical speciation: While the methane experiment will contain only  $\text{CH}_3\text{O}_2$  and  $\text{HO}_2$ , the 1-butene system contained  $\text{C}_2\text{H}_5\text{O}_2$  and  $\text{CH}_3\text{O}_2$ , please give the precise response factors to the different  $\text{RO}_2$  radicals. Is the  $\text{ROxLIF}$  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,  $\text{C}_2\text{H}_5\text{CHOO}$  and  $\text{CH}_2\text{OO}$ , which may be present ?

-To what extent was the intercomparison conducted in a blind manner, as in the recent  $\text{HOxCOMP}$  campaign ?

#### Other Comments

-A key aspect of the LIF  $\text{HO}_2$  detection is that there is insufficient time (or  $[\text{O}_2]$ ) for  $\text{RO}_2$  to be converted to  $\text{OH}$  by reaction with the added  $\text{NO}$  within the LIF system low pressure region; this point should be made in the  $\text{ROxLIF}$  description.

-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  $\text{ROxLIF}$  system; are there any data regarding effects of wall proximity on radical levels in such chambers or with this system ?

-The large methane mixing ratio present in the chamber will compete with  $\text{CO}$  for reaction with  $\text{OH}$  in the  $\text{ROxLIF}$  reduced pressure  $\text{RO}_2$  conversion section; I calculate that ca. 10 % of the  $\text{OH}$  will react with  $\text{CH}_4$  rather than  $\text{CO}$  at the levels given ( $\text{CO}$ , 0.17%;  $\text{CH}_4$ , 0.5%). Will this affect the  $\text{ROxLIF}$  measurements ?

-In the conclusions section, the retirement of the Jülich MIESR system is discussed.

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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.

### Typos / Minor comments

English usage in general could do with revision for style although the meaning is clear enough.

p.377 Only certain VOCs are oxidised by NO<sub>3</sub>. Define NO<sub>x</sub>.

p.377 Line 8; The NO<sub>x</sub> steady state does not affect O<sub>3</sub> \*once steady state is achieved\*, but the initial titration of O<sub>3</sub> by reaction with exhaust-derived NO does lead to changes in NO/NO<sub>2</sub>/O<sub>3</sub>; 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.382 line 13 Strictly you cannot achieve complete chemical conversion, rather the HO<sub>2</sub> undergoes an exponential decay

p.388 Strictly the RO<sub>2</sub> levels are not \*entirely\* controlled by the O<sub>3</sub> / alkene levels as they undergo self- and cross-reactions also (plus HO<sub>2</sub>+O<sub>3</sub>).

p.391 line 7 allowed the design of

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