

Interactive comment on “Detection of HO₂ by laser-induced fluorescence: calibration and interferences from RO₂ radicals” by H. Fuchs et al.

Anonymous Referee #1

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The paper by Fuchs et al. is very interesting indeed. This study was overdue and it is a very important contribution to the understanding and interpretation of HO₂ measurements in the atmosphere. The paper immediately puts into question HO₂ measurements which have been made using chemical titration to OH radicals with subsequent detection of the additional OH generated by LIF spectroscopy, or in fact any other indirect chemical method involving conversion of RO₂ or HO₂ radicals by reaction with NO followed by subsequent measurement of some species (e.g. H₂SO₄ after conversion to OH).

As can be seen from the two Interactive Comments, other groups have conducted related experiments with a range of alkanes and alkenes, both in terms of yields for HO₂ from decomposition of RO₂ radicals, and the degree of interference from RO₂

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radicals on HO₂ measurements using real field instrument setups.

Unless speciated field measurements of RO₂ are available (which they are not), it is going to be impossible to subtract any interference empirically. Modelled speciated RO₂ values could be used, and with knowledge of the interference for specific RO₂ species for a given experimental system, the HO₂ signals could be corrected, but this would be a dangerous exercise given the likely uncertainties in the model.

It is also clear from this paper that the relative interference from RO₂ towards the HO₂ signal will be quite dependent on the individual set up, with NO concentration, reaction time (pumping speeds and volumetric flow rates through the pinhole differ a lot from group to group), and efficiency of mixing of NO into the jet (dependent upon many things) all being important factors. It is important now that each group which uses a method that is potentially affected by this interference undertakes detailed characterisation experiments to assess the precise level of interference (see the Interactive Comments for example), and that this is published in the peer reviewed literature.

This paper has also looked at the implication of the new interferences on previous measurements of HO₂ radicals made by the Julich FAGE instrument. For the PRIDE China project, in fact any correction would make the difference between the measured HO₂ concentrations and those calculated from a constrained box model even larger, highlighting an even bigger role to be played by unknown chemical processes in this environment. For other studies, the interference could help to explain some of the discrepancies that are seen between measurements of HO₂ and models, but unless speciated RO₂ is known (which it is not), it will not be possible to quantify the correction accurately and reassess the situation, although in broad terms it would be possible to say if conclusions were still valid

Interestingly, the decomposition of beta hydroxyl-alkoxy radicals to HO₂ is a known mechanism, with details available in the MCM, and indeed has been discussed informally before in terms of giving an interference for HO₂ conversion in LIF instruments.

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So it is perhaps surprising that it has taken the community so long to definitively show this is occurring, hence the importance of this paper. Interferences from small alkane derived RO₂ species have been shown in the past (and published) not to constitute an interference for HO₂ measurements, but the study was not extended to higher alkanes or alkenes. So it is very timely for this group to have shown definitively that this type of RO₂ does present an interference. This paper will hopefully provide the impetus for groups to characterise their respective instruments, and it provides some insights into how a change in the design may minimise any interferences in future field experiments.

An additional result from this paper was the confirmation that the ratio of HO₂ to the sum of OH plus HO₂ formed following the photolysis of water vapour at 185 nm in air is indeed 0.5. This is an important result, as it represents an assumption made by every group that utilises the mercury photolysis of water vapour to generate OH and HO₂ radicals for calibration of field instrument. It is perhaps a relief that the value is indeed 0.5! The methodology using CD₄ was very neat. The paper also provides some experimental evidence that the losses in the inlet itself (heterogeneous) are larger for OH than for HO₂ – not surprising, but not before shown definitively for FAGE instruments.

The paper is very carefully written, and the level of detail is exemplary. The paper reports the relative RO₂ sensitivity compared with the HO₂ sensitivity for their field setup, together with a different one with a smaller pinhole. The fact that the two sets of experimental conditions lead to quite a big difference in the level of interference, shows that any effect is likely to be quite dependent on the precise design and operating conditions of different FAGE instruments that are currently in operation.

This paper makes important observations and will have a significant impact on parts of the atmospheric measurement community, and I fully support publication in AMT.

More specific comments and questions.

It is unclear from the paper whether the hydrocarbons are added to the calibration gas mixture before the Hg lamp or after it. In Fuchs et al 2008, in which the RO₂ measure-

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ment technique which uses the conversion of RO₂ into HO₂ followed by detection of HO₂ using the chemical conversion method with NO is described, it would seem that the parent hydrocarbons are added before the lamp. If this is the case, the authors should discuss possible photolysis of the alkenes in this present study which may lead to the formation of RO₂ or HO₂ and impact on the interference measurements. Ethene for example might be expected to undergo some photolysis to generate an H atom which then generates HO₂ quickly in air. Previous studies (e.g. Giroux et al., Can. J. Chem. 67, 1166, 1989, and many others) discuss yields of H atoms at 193 nm, and there have been studies at 185 nm. It may be difficult to distinguish between an HO₂ interference from RO₂ decomposition and photolytic sources of HO₂.

As raised by both Dillon and Whalley in their Interactive Comments, higher alkanes (>C₃) also rapidly convert in the presence of NO and generate HO₂. This should be mentioned in the paper, which suggests that there is no interference for “small” alkanes. In response to the Interactive Comment from Mainz, an RO₂ to HO₂ conversion via a Peeters’ type mechanism may not be discernible from HO₂ generated as a result of an RO₂ interference during the detection of HO₂, if the RO₂ species itself is detected with a similar efficiency to HO₂.

In the abstract it is noted that there are unlikely to be interferences in “clean air”. This is confusing and possibly a bit misleading, as a low NO_x environment, such a remote rain-forest, where there are high levels of isoprene, and therefore potentially an interference in HO₂ measurements, would be considered by many people as a “clean” environment. “Remote clean environment with no significant emissions of biogenic VOCs” would be better.

Page 1261, line 24, the authors should mention the impurities in the NO that lead to artificial signals and are removed by Ascarite.

Page 1263, line 9, Creasey et al (GRL, 2000) also measured the absorption cross-sections for O₂ for a variety of lamps, and for H₂O vapour.

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Page 1265, line 12, “proves” rather than “proofs”

Page 1272, line 15, 1×10^8 was used in the model, earlier it is stated that 7×10^9 are typical radical concentrations used. Perhaps the initial modelled concentration is not critical, but some further statement needed?

Page 1273, line 11. Creasey et al (Appl. Phys. B. 1997) also showed that for a 0.2 mm (flat) nozzle, the rotational temperature had reached room temperature by about 40-50 mm downstream of the inlet nozzle.

Page 1283, second bullet point line 16-19, “small” should be defined more carefully, as other studies seem to indicate that there is an interference for larger alkanes.

Page 1284, line 5, “at the expense of” would be better than “on the cost of”

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 1255, 2011.

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