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Atmospheric measurements of peroxy radicals by chemical amplification

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Peroxy radicals (HO_2 and RO_2) are key species in atmospheric chemistry. They are produced during the oxidation of volatile organic compounds (VOCs) and are involved in the formation of ozone and secondary organic aerosols. However, ambient measurements of these reactive species are still considered challenging and only a few techniques have been used for field measurements. Among these techniques, the PEroxy Radical Chemical Amplifier (PERCA) implementing the classical NO/CO reagent approach has been hardly used for field measurements due to the strong dependence of the radical chain length on Relative Humidity (RH). However, Wood et al. (ES&T 2016) recently showed that using ethane instead of CO allows reducing this RH-dependence and helps going around other drawbacks of the CO based amplification chemistry.

This new approach has been explored in our laboratory by building a PERCA instrument that will be used for both laboratory kinetics and field measurements. In this presentation, we will describe (i) the measurement setup and (ii) experiments conducted to quantify the radical chain length for HO_2 and several RO_2 radicals, including those produced during the OH-oxidation of isoprene, toluene, cyclohexane, and others. It will be shown that the detection efficiency of organic peroxy radicals, via their NO conversion to HO_2, mainly depends on their organic nitrate ($RONO_2$) formation yields. In this context, box modelling of the PERCA chemistry will be discussed.