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Intercomparison of peroxy radical measurements by laser-induced fluorescence and electron spin resonance spectroscopy at the atmosphere simulation chamber SAPHIR

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Two experiments were carried out at the atmosphere simulation chamber SAPHIR in Jülich, Germany, in order to compare measurements of atmospheric hydroperoxy radical (HO_2) and organic peroxy radical (RO_2) concentrations by two different techniques. The first technique was the well-established Matrix Isolation Electron Spin Resonance (MIESR), which provides absolute measurements with a time resolution of 30 min and high accuracy (10 %, 2 σ). The second was the newly developed ROxLIF instrument, which detects peroxy radical at a temporal resolution of 1 min and an accuracy of 20 % (2 σ). It is based on the selective chemical conversion of $\mathrm{RO_X}$ radicals (HO_2 and RO_2) to OH, which is detected with high sensitivity by laser-induced fluorescence (LIF). Quantitative photolysis of water vapor at 185 nm is used in order to calibrate measurements of the ROxLIF instrument. Two complementary types of atmospheric simulation experiments were carried out, during which atmospheric concentrations of peroxy radicals within the range of 16 to 100 pptv for HO_2 and 12 to 45 pptv for RO_2 were produced. In one experiment, HO_2 and CH_3O_2 radicals were produced by photooxidation of methane in air. In the second experiment, HO_2 and $C_2H_5O_2$ were produced by ozonolysis of 1-butene in air at dark conditions. Measurements of both instruments, ROxLIF and MIESR exhibit good agreement within their combined experimental uncertainties. Linear regressions to the combined data set yield slopes of $1.02 \pm 0.13 (1\,\sigma)$ for RO_2 and $0.98 \pm 0.08 (1\,\sigma)$ for HO_2 without significant offsets. The results confirm the calibration of the ROxLIF instrument and demonstrate that it can be applied with good accuracy for measurements of atmospheric peroxy radical concentrations. H. Fuchs et al, Atmos. Meas. Tech. Discuss., 1, 375-399, 2008.