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Supplement of

ROOOH: a missing piece of the puzzle for OH measurements in low-NO environments?

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- 1.) FAGE pump and probe system
- 2.) LIF calibration procedure
- 3.) Complementary measurements with CH_3COCH_3 : detection of interferences due to a 2-photon process
- 4.) Global model simulations with varying ROOH loss rates

1.) FAGE pump and probe system

Details of the ULille FAGE pump and probe system have been described in detail elsewhere publications (Fuchs et al., 2017; Hansen et al., 2015; Parker et al., 2011)

Briefly, the FAGE instrument is coupled to a photolysis cell (**Figure S1**), in which a plume of OH is generated by 266 nm photolysis of ozone in presence of water vapor. Time-resolved OH decays are monitored at a temporal resolution of 200 μs using the high repetition rate probe laser (5 kHz) of the FAGE instrument. The photolysis cell is a 50-cm long, 5 cm-i.d. cylindrical tube made of aluminum. A Suprasil quartz window is mounted on one side of the cell, and the other side is directly connected to the FAGE nozzle. The pressure in the photolysis cell is around 745 Torr, and pumping from the FAGE instrument (3 L min^{-1}), the O_3 analyzer (0.3 L min^{-1}) and the hygrometer (0.4 L min^{-1}) ensures that the photolysis cell is continuously flushed with gas mixture. The residence time within the photolysis cell is around 20 sec, *i.e.* at a photolysis repetition rate of 2 Hz, the gas mixture is photolysed around 40 times before it enters the FAGE detection cell. Experiments have been carried out by first covering the photolysis laser in order to start each series with a fresh mixture.

OH is generated inside the cell by ozone photolysis at 266 nm in the presence of water vapor (reactions (RS1) and (RS2)) using a quadrupled YAG laser (Quantel, YG 981C) operated at a pulse repetition rate of 2 Hz.



An ozone mixing ratio of at least 600 ppbv is maintained inside the photolysis cell by injecting a small flow rate of 20 mL min^{-1} (negligible compared to the main flow through the reactor) of concentrated ozone using an ozone generator (Scientech). A water vapor mixing ratio of about 12000 ppmv is injected in the cell by passing a part of the air through a bubbler. The energy of the photolysis laser was set to 20 mJ pulse^{-1} for a beam diameter of 2.5 cm, which was achieved after expansion through a telescope. This expansion of the beam allows the generation of OH in a cylindrical volume that is larger than the FAGE nozzle (0.4 mm) in order to probe a more homogeneous volume with respect to the OH concentration, even if the shape of the beam involves a Gaussian distribution. The pulse duration of the photolysis laser is 20 ns (full-width half maximum).

The photolysis cell is coupled with an airtight connection to the FAGE nozzle where OH is measured by LIF (Laser Induced Fluorescence) using the $\text{Q}_1(3)$ transition ($\text{A}^2\Sigma_+(v=0) \rightarrow \text{X}^2\Pi(v=0)$) at 308 nm after gas expansion into a low pressure cell (0.3 mbar). The laser light is generated using a frequency-doubled dye laser (Sirah Laser PrecisionScan PRSC-24- HPR) pumped by the frequency-doubled output of a Nd:YVO₄ laser (Spectra Physics Navigator II YHP40- 532QW). The laser power used to probe OH was approximately 2 mW.

Hydrocarbons are added to the photolysis cell through calibrated flow meter, either directly from the gas cylinder (CH_4 and $n\text{-C}_4\text{H}_{10}$ for a series of experiments) or from a canister in which a diluted gas mixture of $n\text{-C}_4\text{H}_{10}$ or isoprene had been prepared manometrically.

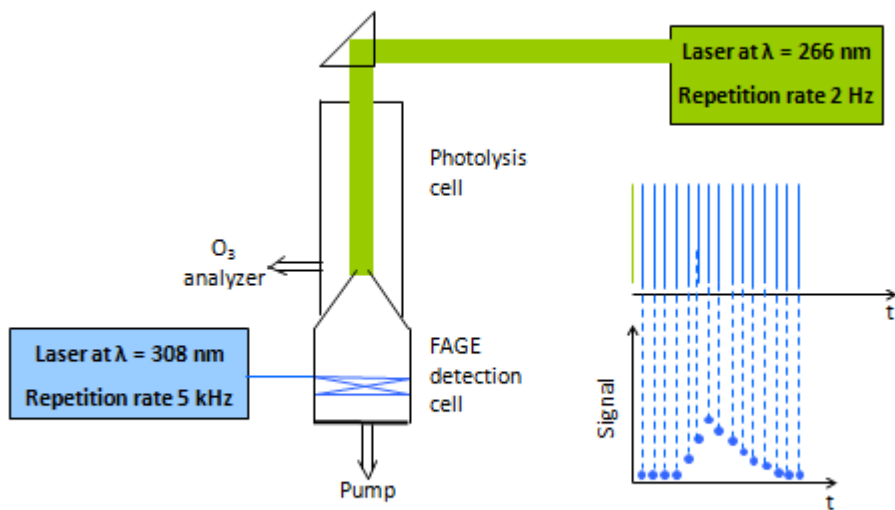


Figure S1: Schematic view of the UL FAGE pump and probe instrument

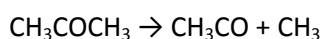
2.) LIF Calibration procedure

In order to access the absolute concentrations of OH radicals, calibrations are made using a calibration cell in which air of known water vapour concentration is photolysed at 184.9 nm by a mercury lamp, producing an equal and known concentration of OH and HO₂. The lamp flux is indirectly measured by actinometry on ozone, produced simultaneously by oxygen photolysis at the same wavelength. For calibration purposes, the photolysis cell is unmounted and the calibration cell is placed in front of the FAGE nozzle. Very high flow of synthetic air (40 l min⁻¹) is flowed through the calibration cell to assure (a) turbulent flow conditions within the calibration cell and (b) that the entire gas intake by the FAGE consists of calibration gas. Details on FAGE calibration procedure can be found elsewhere (*Dusanter et al., 2008*).

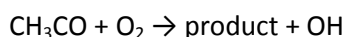
3.) Complementary experiments with CH₃COCH₃: detection of interference due to a 2-photon process

In order to check whether the observed increase in background fluorescence is a 1- or 2-photon process, i.e. due to interference by photolysis or by decomposition of an unknown species, we have carried out experiments with isoprene at the same condition (concentration and photolysis energy) but varying the fluorescence excitation laser energy and/or the repetition rate of the excitation laser.

In order to characterize the refreshing time in our FAGE instrument and to determine if photolytic interferences can be clearly identified, we have used acetone, CH₃COCH₃, known to lead to photolytic interference in the FAGE cell (17), in separate experiments as tracer for OH radicals generated photolytically by the excitation laser within the FAGE cell. Acetone is photolysed at the excitation laser wavelength (308 nm):



with CH₃CO leading in subsequent reaction with O₂ to fast formation of OH with a yield close to 1 at zero pressure (Carr et al., 2007):



If the gas mixture in the excitation volume is not completely renewed between two shots (200μs), the OH radicals formed this way can be excited with one of the next excitation laser pulse. The resulting fluorescence intensity should (a) not be linear with the excitation laser fluence and (b) should decrease with decreasing repetition rate. This has been tested in our system with acetone:

- a.) Clean air containing stable concentration of CH₃COCH₃ is pumped into the FAGE cell, and the resulting fluorescence intensity is plotted as a function of the laser power. **Figure S2** clearly shows a non-linear increase in fluorescence signal with laser power.

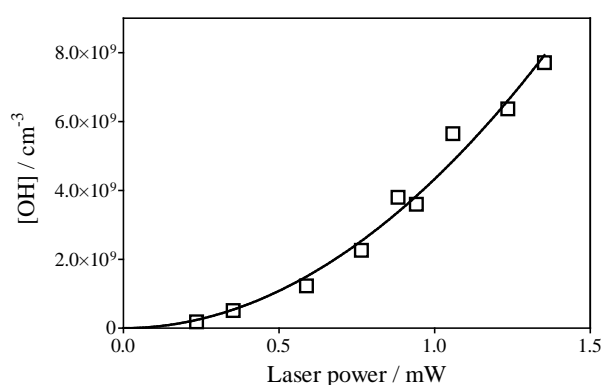


Figure S2: Formation of OH radicals from 308 nm photolysis of CH₃COCH₃ within the FAGE detection volume as a function excitation laser energy within the FAGE cell. Repetition rate of the dye laser was 5 kHz, [CH₃COCH₃] = 1.5 × 10¹⁶ cm⁻³. Black line shows square dependence of OH signal with the excitation laser energy

- b.) Clean air containing stable concentration of CH₃COCH₃ is pumped into the FAGE cell, and the resulting fluorescence is measured at different excitation laser repetition rates. In these

experiments, the pump laser energy has been adapted to obtain the same pulse energy for different repetition rates. It can be seen that the OH concentration decreases, but even at 1 kHz, i.e. 1 ms between two excitation laser pulses, there is still a small OH signal is observed, as shown in **Figure S3**.

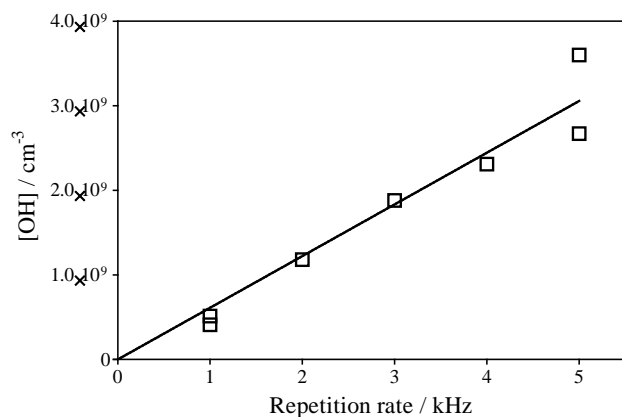


Figure S3: Formation of OH radicals from 308nm photolysis of CH_3COCH_3 as a function of the repetition rate. The YAG-laser energy has been adjusted in order to obtain for all repetition rates the same energy (0.8 mW within the FAGE cell). $[\text{CH}_3\text{COCH}_3] = 1.3 \times 10^{16} \text{ cm}^{-3}$.

From these experiments, it can be deduced that in the UL FAGE photolytically generated OH radicals can be identified by either varying the fluence or the repetition rate of the fluorescence excitation laser.

4. Global model simulations with varying ROOOH loss rates

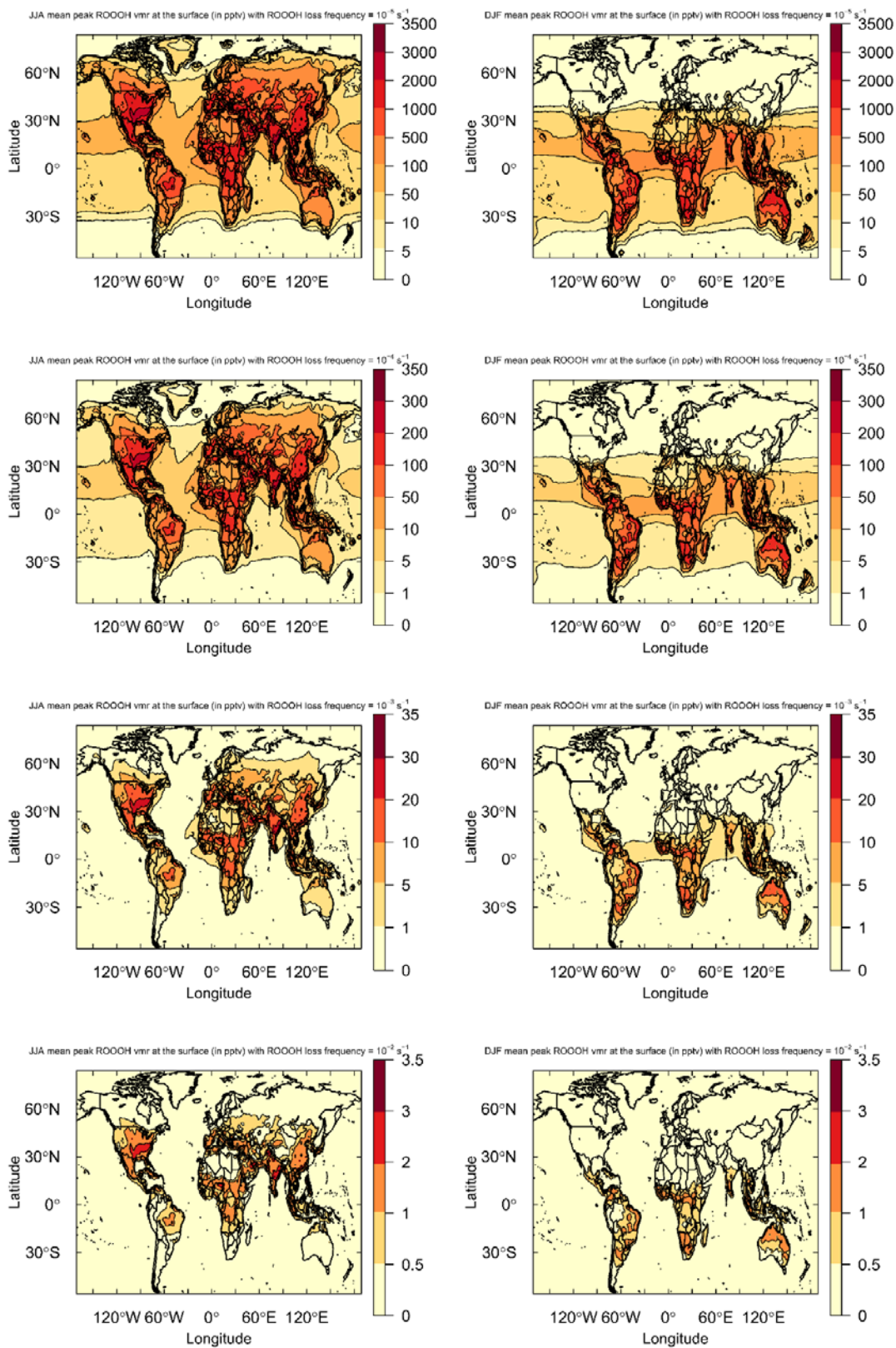


Figure S4: Modelled mean diurnal peak ROOOH volume mixing ratio (in ppt) during the Northern (left hand side) and Southern (right hand side) summer months. Each row shows steady state ROOOH abundances obtained with different ROOOH removal rates, ranging from 10^{-5} to 10^{-2} s^{-1} .

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