

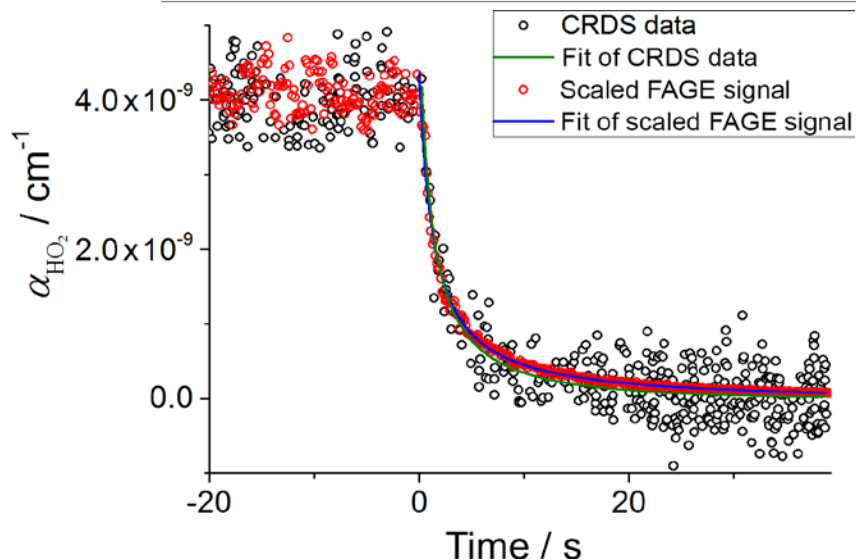


Milestone 10.8

Milestone 10.8: Prototype of new instrumentation for the detection of hydroxyl radicals, hydroperoxy radicals and speciated organic peroxy radicals developed

Achievements:

- New instruments for HO₂ and CH₃O₂ detection based on cavity ring-down spectroscopy (CRDS) developed for HIRAC (NCAS-Leeds)
- New instruments for radical detection based on chemical ionization mass spectrometry (CIMS) in HELIOS (CNRS-ICARE), in LEAK-LACIS (TROPOS) and in SAPHIR (FZJ)
- New chemical modulation system developed for OH instrument based on laser-induced fluorescence (LIF-CHEM) in SAPHIR (FZJ)

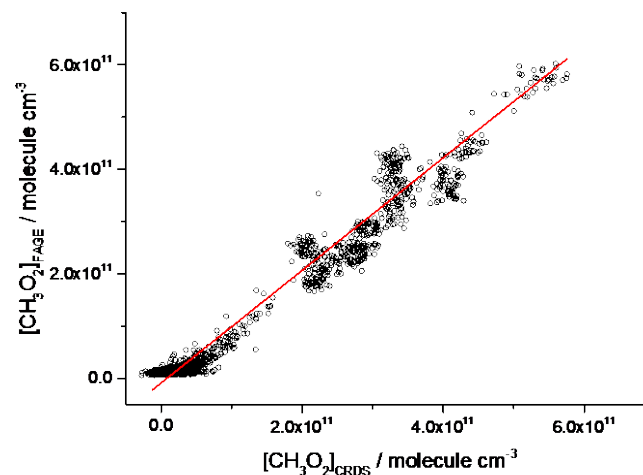
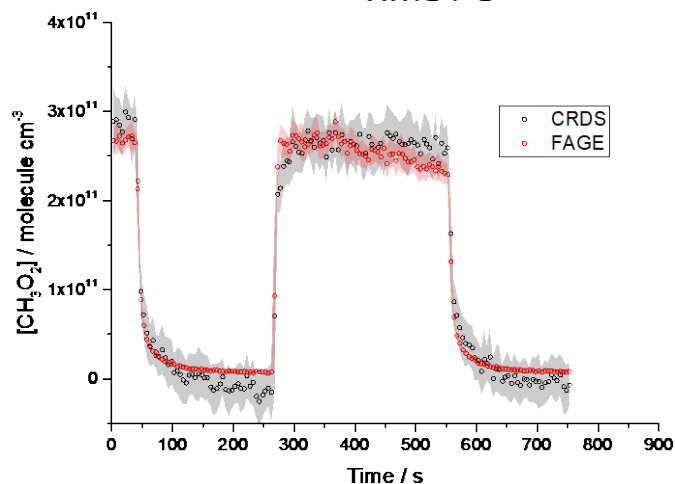


Comparison of HO₂ temporal profiles from CRDS and FAGE

Onel, Atmos. Meas. Tech, 2017

Equivalent comparison for CH₃O₂ and
Regression plot (grad 1.08 ± 0.03). Paper
in preparation (for AMT)

Kinetics studies on CH₃O₂ self reaction &
cross reaction with HO₂ in progress.
Publication planned in near future.



- Set-up of a NO_3^- -CI-API-TOF mass spectrometer modified according to Eisele and Tanner (1993) to measure and quantify OH radicals
- Based on the reaction of SO_2 to H_2SO_4
- $[\text{H}_2\text{SO}_4]$ is measured and serves as measure for OH-radicals
- First experiments were performed to evaluate the influence of the OH radicals source on the quantification results:

Photolysis of H_2O_2



Dark formation of H_2SO_4

Photolysis of O_3

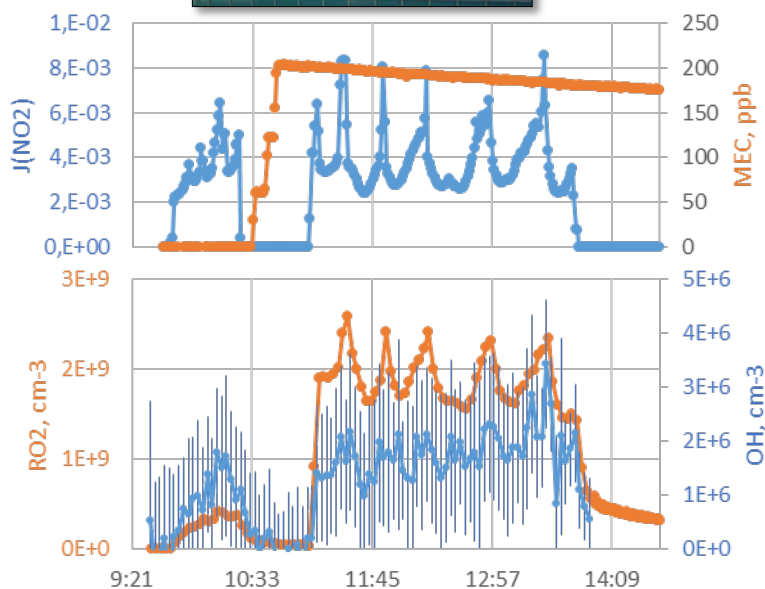
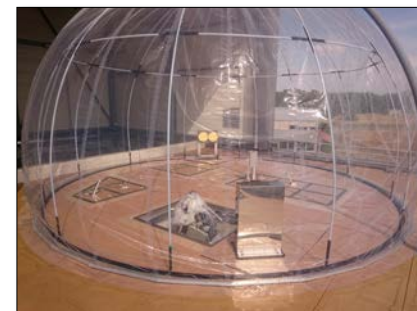


Influence of Criegee Intermediate negligible

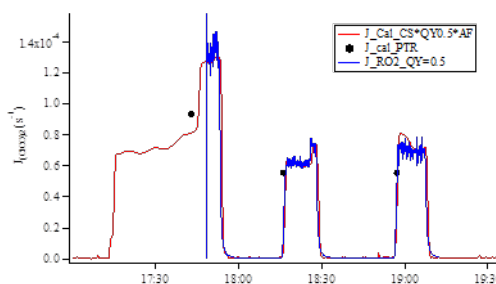
Ozonolysis of TME



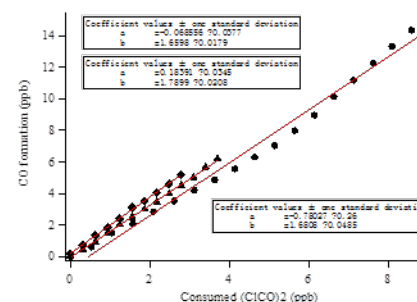
Successful coupling of a Chemical Ionization Mass Spectrometer (SAMU) to HELIOS for OH/RO₂ radicals during the photolysis of different chemical systems

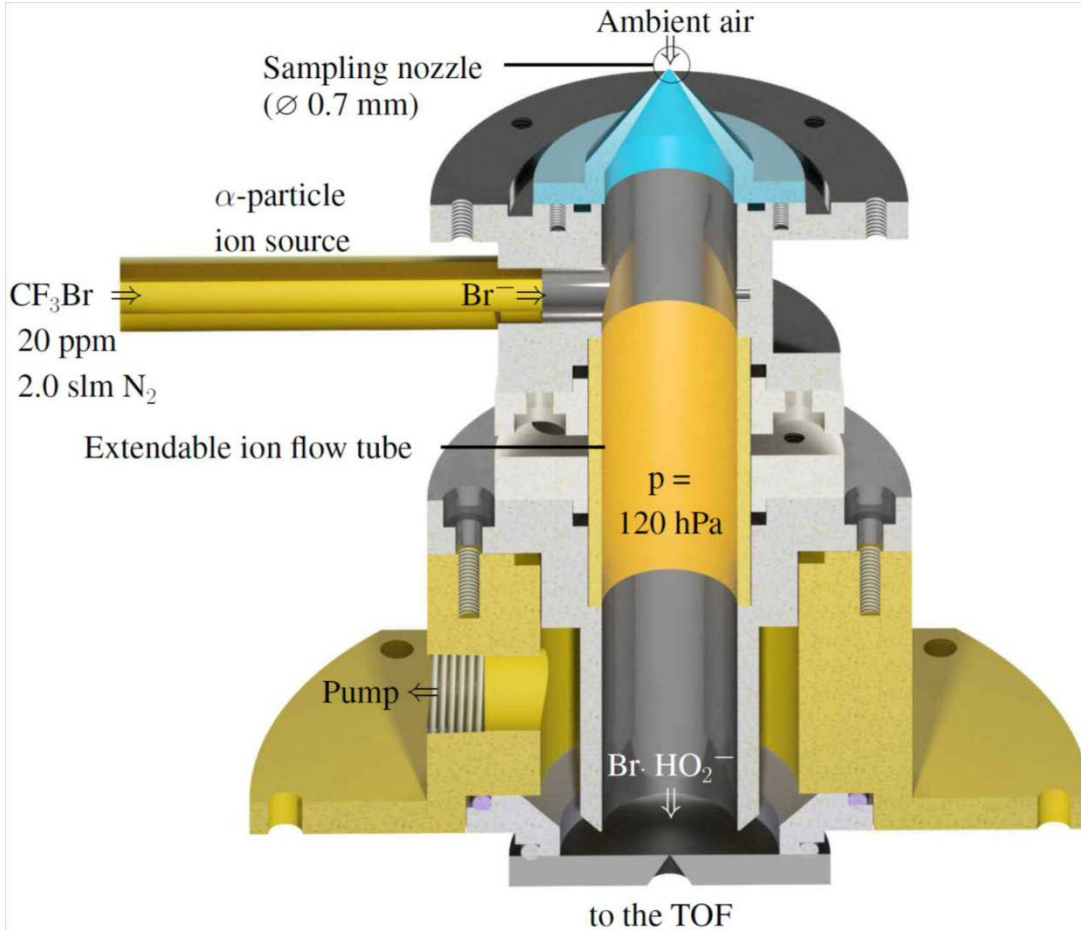


OH and RO₂ from MEK photolysis



OH and RO₂ from (ClCO)₂ photolysis in the presence of H₂, CH₄, CH₃CH₃

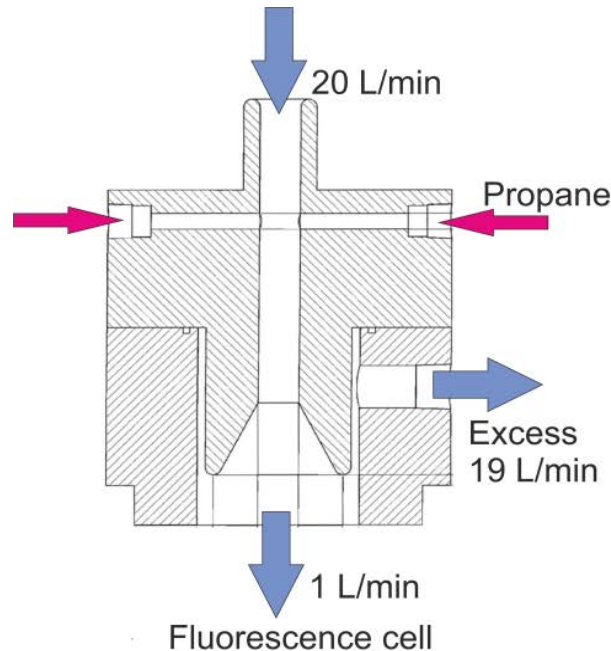




Detection of HO₂ as cluster with Br⁻ by Chemical Ionization Mass Spectrometry (CIMS)

- Direct detection without chemical conversion to OH like in other instruments
- High sensitivity (detection limit $\sim 4 \times 10^7 \text{ cm}^{-3}$)
- Concurrent HO₂ measurements of the CIMS and established LIF instrument in the SAPHIR chamber results in a good agreement.

Albrecht, Atmos. Meas. Tech. Discuss., 2018



Chemical modulation system for OH detection by laser-induced fluorescence in photochemistry experiments in SAPHIR

- Addition of OH scavenger propane upstream of sampling nozzle
 - Distinguish between OH in the chamber and OH internally produced in the measurement cell
 - Ensuring that OH measurements are not affected by artifacts

Test experiment demonstrating the performance of the chemical modulation system:

- Ambient OH is present during phases with roof open, no OH is expected during phases with roof closed
- Ambient OH is detected in the absence of the OH scavenger (blue dots)
- Internally produced OH would occur in the presence of the OH scavenger (red dots), but no interference was detected in this experiment

