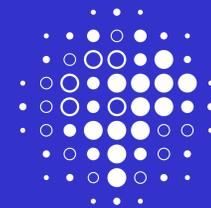


Development of an airborne OH reactivity instrument based on the pump probe technique

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Abstract

The removal of OH radicals to all sinks in the troposphere can be defined by its total pseudo first order loss rates coefficient (k_{OH}) and which is generally termed as total OH reactivity. Several techniques had been developed to measure this quantity. We have been developing an instrument for measuring OH reactivity in the troposphere by using laser flash photolysis combined with laser induced fluorescence (LFP-LIF) technique. We did laboratory experiments to demonstrate the performance of OH reactivity instrument. We observe in the first 200 msec almost no wall loss with an average k_{OH} value for zero air decay of $\sim 0.5 \pm 0.5 \text{ sec}^{-1}$. In order to verify the accuracy of the measured decay rates, methane and propane were added to the zero air and the resultant decay rates compared with the calculated decay rates using the recommended rate constant. The experimentally measured k_{OH} values agrees well with the calculated ones. In addition, results from the influence of humidity, O_3 and NO on the total OH reactivity measurements will be presented.

Experimental setup

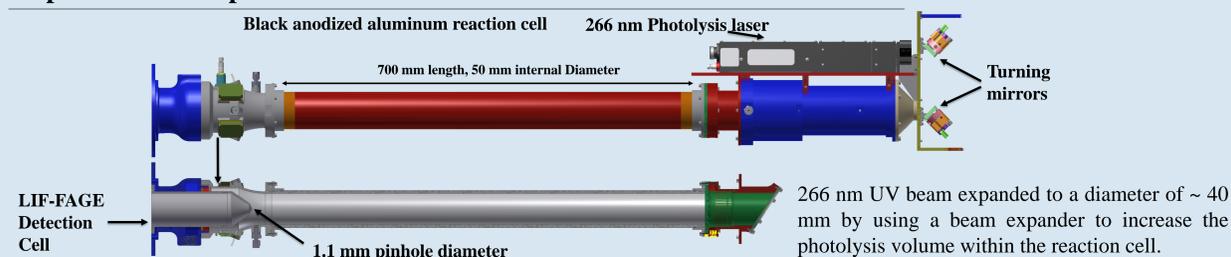


FIG.1 Schematic diagram of the reaction cell with photolysis laser

- 1 Hz repetition rate of the photolysis laser at 266 nm while OH is sampled with a rate of 3 kHz at 308 nm
- ~ 90 slm of air sampled through the flow tube (FT), measured by a low dP mass flow meter, to ensure a complete air exchange before the next photolysis pulse is fired.
- ~ 5 -10 slm of zero-air/synthetic-air bubbled through a distilled water container to get moist air and then mixed with ~ 90 slm of zero-air/synthetic-air.
- O_3 is generated in a 100 scem O_2 flow by photolysis at 185nm in a Suprasil glass tube leading to ~ 20 -50 ppbv O_3 inside the flow tube.
- The pressure inside the flow tube is ~ 30 hPa below ambient, the temperature is kept at 25°C for the present experiments.
- Water vapor, O_3 , NO, Pressure and Temperature are continuously monitored in the FT.

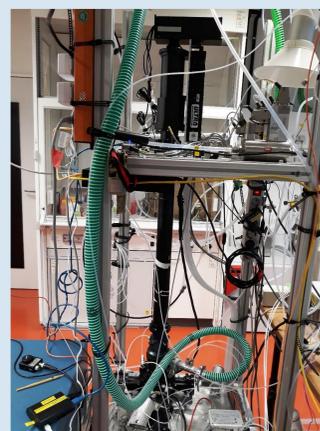


FIG.2 Snapshot of the OH reactivity setup in our laboratory.

Background estimation using Zero-Air Decays

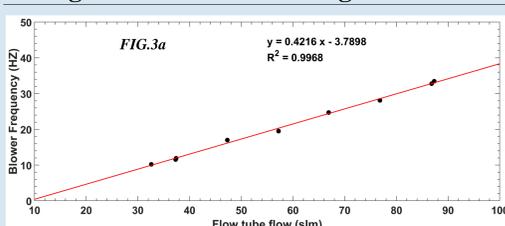


FIG.3a: The flow rate inside the flow tube is controlled by a blower and calibrated by balance flow method. The residence time inside the 70 cm FT with 50 mm inner diameter at a flow of 90 slm is ~ 1 sec.

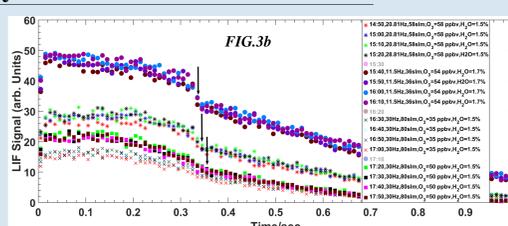


FIG.3b shows measured decay profiles of zero air with different flow speeds. In the first 200 msec almost no wall loss was observed. Under pseudo first order conditions, the decays were fitting within the first 200 ms using following expression

$$[OH]_t = [OH]_{t=0} \exp(-k_{OH}t)$$

The effect of double pulsing the sample in the flow tube is studied. A sharp drop high-lighted by black arrows in OH concentration can be seen in the beginning of a decay with low flow speeds (36 slm). Increasing the flow speed up to 80 slm leads to a smaller and delayed drop.

FIG.3c: k_{OH} values as a function flow in the FT shows no dependence on k_{OH}

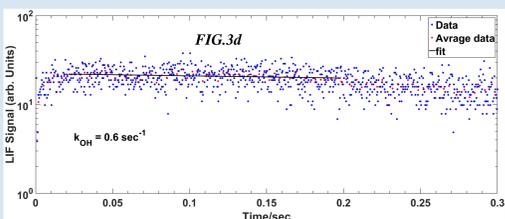
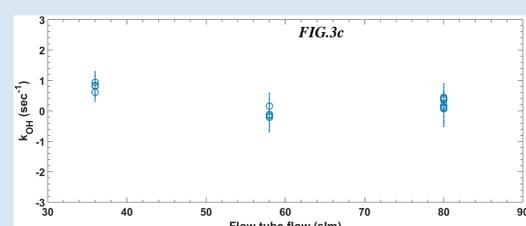


FIG.3d shows one of the typical zero air decay of our instrument with a time resolution of 333 μs . The corresponding k_{OH} is 0.6 sec^{-1} .

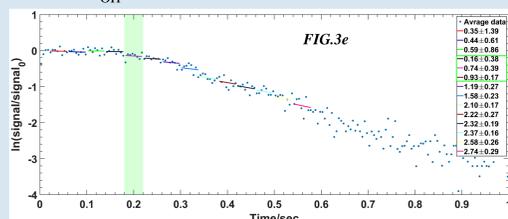


FIG.3e: The time until wall loss occurs in our system is determined to be 0.18-0.22 sec by fitting small sections of a measured zero air decay and test the change in slope with a 95% confidence level. The zero air decay with wall loss after 0.24 sec is $5.9 \pm 0.5 \text{ sec}^{-1}$.

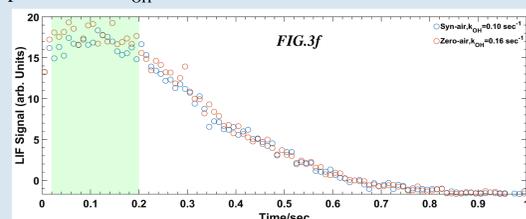


FIG.3f: Comparison of OH decay profiles between synthetic air (Westfalen) and zero air (generated from AIR PURIFIER CAP 180). Both decays are very similar and the decay rates are in very good agreement with each other

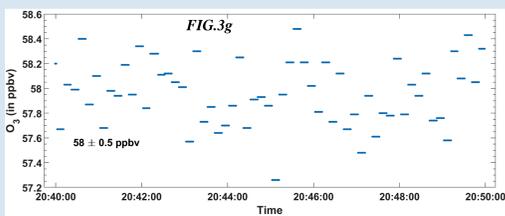


FIG.3g and 3h: The variability of the O_3 and H_2O vapor concentrations during laboratory experiments is less than 1%.

Abbreviations

FT: Flow tube
 NO_x : NO+ NO_2

Verification of the accuracy of the measured OH decay rates

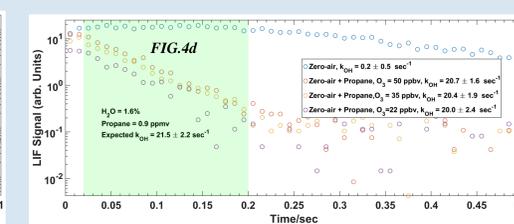
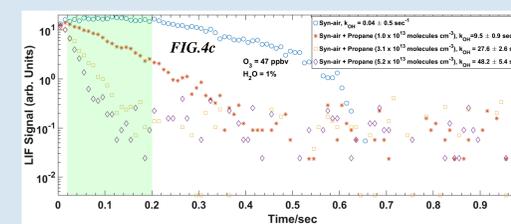
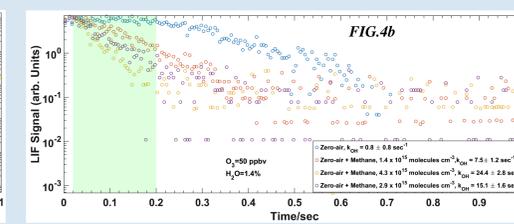
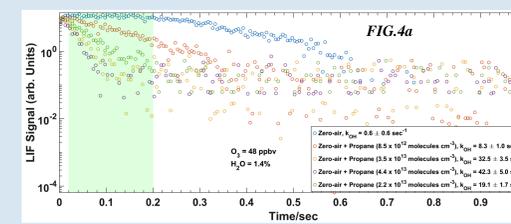


FIG.4e: The statistical uncertainties of our measurements are ~ 10 -15%, while for theoretically obtained values using error propagation method yielded $\sim 10\%$ uncertainty. The expected OH decay rates are calculated using IUPAC recommended rate constants. Temperature, pressure, and concentration of the hydrocarbons, are taken from measurements in the flow tube. Good agreement between the measured and theoretically calculated OH reactivity is found ($R^2=0.9964$).

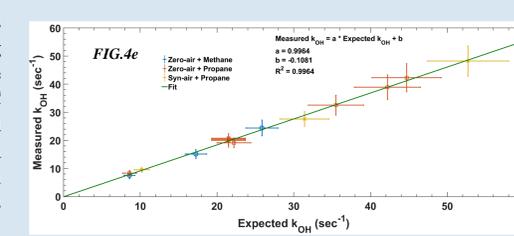
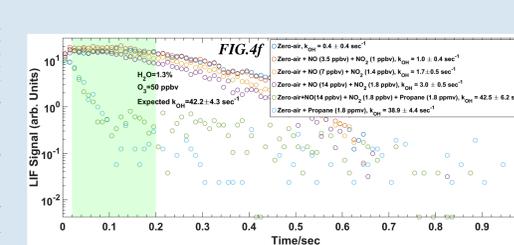
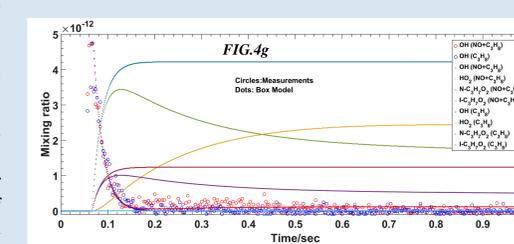


FIG.4f: The OH reactivity shows a faster decay with increase in NO mixing ratios in the FT. Reactions of OH radicals with NO and NO_2 contribute to the total OH decay rate. The expected OH reactivity due to NO (14 ppbv) and NO_2 (1.8 ppbv) are 2.3 sec^{-1} and 0.4 sec^{-1} , respectively (calculated using IUPAC recommended rate constants). The measured OH reactivity due to NO_x (15.8 ppbv) is 3.6 sec^{-1} (difference between light green and blue circles). The decay of zero-air shows a faster decline. The results are in good agreement with the calculated OH reactivity rate due to 15.8 ppbv NO_x (2.7 sec^{-1}).



The calculated OH reactivity under different NO_x mixing ratios are 0.8 sec^{-1} (red circles), 1.5 sec^{-1} (orange circles), and 3 sec^{-1} (violet circles). Thus we conclude that at high ambient NO conditions, the true OH reactivity is overestimated. The time scale is sufficient short ($< 0.2 \text{ sec}$) for the effect of RO_2 recycling into OH within the uncertainty of the measured and expected reactivity. However, at later time enhancement in the LIF OH signal indicates OH recycling from secondary reactions.



Summary and Future work

- In this work we developed and characterized an OH reactivity instrument in our laboratory using laser flash photolysis combined with laser induced fluorescence (LFP-LIF) technique to be deployed for wide ranges in hydrocarbon and NO_x variations during field campaigns.
- Impact of wall loss is observed to be less than 1 sec^{-1} for zero-air/synthetic-air decays in the first 200 msec.
- The measured OH reactivity values are in good agreement ($< 8\%$) with the theoretically estimated ones.
- The influences of NO_x and O_3 on OH reactivity have been estimated.
- The effect of OH recycling on measurement of OH reactivity at high ambient NO_x environment needs further investigation.
- Optimum operation conditions for airborne measurements will be determined from laboratory experiments and model simulations.

FIG.4a-d: The accuracy of the measured decays rates have been verified with different concentrations of methane and propane. Measured OH decays rates are in good agreement ($< 8\%$) with the theoretically calculated OH reactivity values up to 53 sec^{-1} .

FIG.4d: OH reactivity for different O_3 concentrations expected to be encountered during field campaigns. Measurements under these conditions show no variation in the reactivity. However, the measured detector signals increase with ozone concentration, thus adding of O_3 yields a increase in limit of detection. Therefore, addition of O_3 improves the OH signal. This is necessary for ambient of $O_3 < 20 \text{ ppbv}$.

FIG.4g: To investigate OH recycling from $HO_2 + NO$ reactions we performed Box model calculations using CAABA/MECCA. The propane, O_3 , H_2O , and NO concentrations are set to match the measurement conditions. OH is initialized to 5 pptv. FIG.4f shows quite good agreement between the measured and model OH decay. Similar to experimental evidence in Fig 4f, enhancement in OH is observed in model simulations. This is due to $HO_2/RO_2 + NO$ reactions.