

## Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS) and Measurement of Atmospheric OH Reactivity (MAOHR)

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### Summary of Proposed Work.

The atmosphere's fast photochemistry is driven by the hydroxyl radical (OH) and the hydroperoxyl radical (HO<sub>2</sub>). It dictates the chemical evolution of pollution plumes. These fast and sensitive OH and HO<sub>2</sub> measurements will test the non-linear photochemistry in these plumes. The OH reactivity is the sum of the product of the concentrations of all atmospheric constituents that react with OH and their reaction rate coefficients. Comparison of the measured OH reactivity to that calculated from measurements of all known reactants tests the completeness of those measurements.

### Instrument Description

#### *ATHOS.*

ATHOS is located in the forward cargo bay. It uses laser-induced fluorescence (LIF) to measure OH and HO<sub>2</sub> simultaneously. OH is both excited and detected with the  $A^2 \Sigma^+(v'=0) \rightarrow X^2 \Pi^+(v''=0)$  transition near 308 nm. HO<sub>2</sub> is first reacted with reagent NO to form OH and is then detected with LIF. ATHOS can detect OH and HO<sub>2</sub> in clear air and light clouds from Earth's surface to the lower stratosphere.

The ambient air is slowed from the aircraft speed of 240 m/s to a controlled 8-40 m/s in an aerodynamic nacelle, and is then pulled by a vacuum pump through a small inlet, up a sampling tube, and into two low-pressure detection cells. The first cell is for OH and the second for HO<sub>2</sub>. Detection occurs in each detection cell at the intersection of the airflow, the laser beam multi-passed with White cells, and the detector field-of-view.

The laser has a 3 kHz pulse repetition frequency, 10 ns long pulses, and is tuned on and off resonance with the OH transition to determine OH fluorescence and background signals. The detector is gated to detect the OH fluorescence after the laser pulse has cleared the detection cell. A reference cell containing OH shows when the laser is on and off resonance with the OH transition.

#### *Measurement of Atmospheric OH Reactivity (MAOHR).*

OH reactivity is measured directly by pulling the ambient air at a known velocity through a cylinder. An OH detection system, similar to the one used in ATHOS, protrudes into the cylinder near its end. A few pptv of OH is added to the ambient air through a probe that moves along the cylinder's axis. As the probe is pulled back, the reaction distance, and thus time, increases and the OH decreases as it reacts. The slope of the logarithm of OH versus time gives the OH reactivity (s<sup>-1</sup>).

ATHOS and OH Reactivity Measurement Characteristics			
measurement	minimum integration time	limit-of-detection	accuracy (2 $\sigma$ , 1 minute)
OH	20 s	0.01 pptv	$\pm 32 \%$
HO <sub>2</sub>	0.2 s to 20 s	0.1 pptv	$\pm 32 \%$
OH reactivity	about 1 s to 240 s	about $< 1 \text{ s}^{-1}$	about $\pm 15 \%$

### Publications about ATHOS and the Measurement of Atmospheric OH Reactivity.

Faloona, I.C., D. Tan, R.L. Lesher, N.L. Hazen, C.L. Frame, J.B. Simpas, H. Harder, M. Martinez, P. Di Carlo, X.R. Ren, W.H. Brune, 2004: A laser-induced fluorescence instrument for detecting tropospheric OH and HO<sub>2</sub>: Characteristics and calibration, *J. Atmos. Chem.*, **47**, 139-167.

Kovacs, T., and W. Brune, 2001: Total OH Loss Rate Measurement. *J. Atmos. Chem.*, **39**, 105-122.

A schematic of ATHOS. Top view is looking aft; bottom view is looking starboard. The OH Reactivity Measurement is in the electronics rack.

