A Cavity-Enhanced Ultraviolet Absorption Instrument for High-Precision, Fast Time-Response Ozone Measurements

Reem A. Hannun^{1,2}, Andrew K. Swanson^{1,3}, Steve A. Bailey¹, **Thomas F. Hanisco¹**, Thaopaul Bui⁴, Ilann Bourgeois^{5,6}, Jeff Peischl^{5,6}, Thomas B. Ryerson⁵, Glenn S. Diskin⁷

 NASA Goddard Spaceflight Center, 2. Joint Center for Earth Systems Technology/UMBC, 3. Universities Space Research Association, 4. NASA Ames, 5. NOAA Earth Science Research Lab, 6.CIRES, 7.NASA Langley

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Motivation

- Ozone dry deposition of ozone is an important loss mechanism
 - Models need accurate representations to predict transport
 - Deposition impacts plant health and crop yields
- Airborne eddy-covariance flux measurements require fast 1 – 10 Hz measurements of ozone with precision ~ 0.1 ppb/s.
- Chemiluminescence can achieve this sensitivity, but instrument is complicated and labor intensive





Develop compact, semi-autonomous UV absorption instrument with precision comparable to Chemiluminescence



The technique is similar to common cavity-based designs. Effective pathlength ~ 100m.

Optical Design features

Mirror R ~ 99.7% The optical cell is ~ 100 m effective optical path length.

Fixed mirrors in the cell. No adjustment is needed.

Detection volume ~ 35 cm³. Flow rate ~ 300 cm³/s. Dispersed flow to minimize pulsing and dead volume.



Instrument Design: Rapid Ozone Experiment (ROZE)



| Specification | Value | | |
|--|---|--|--|
| Size | 60 x 44 x 18 cm | | |
| Weight | 19 kg | | |
| Power | < 200 W | | |
| Data rate | 10 Hz | | |
| Precision (1 σ -1s) | 6.7 x 10 ⁸ molec. cm ⁻³ | | |
| Accuracy | 6.2% | | |
| Time response | 50 ms | | |
| RDZE is thermal vacuum tested up to 70 kft | | | |

Operated from -20 °C to > 40 °C

Data Acquisition



Yellow: LED Modulate signal (90% duty cycle, 1 kHz)

Pink: Amplified PMT signal

Blue: Averaging windows for LED ON and OFF

Signal = Mean(ON) – Mean(OFF) 1 kHz averaged to 10 Hz

Calibration



OZONE: calibration using commercial (2Btech) ozone source

Air: calibration using air (Rayleigh scattering extinction)

Precision and Time response



Allan deviation plot for 1.5 hr of sampling zero air at constant pressure (944 mbar).

ROZE time response: High ozone air was injected into the flow system via a pulsed valve (10 ms open time) with a sample flow of 18 SLM.

Field Demonstration



FIREX-AQ July 30, 2019

ROZE and NOyO3 measurements of O3 from the FIREX-AQ field campaign averaged to 1 second. For 14 other FIREX-AQ flights, slopes ranged from 0.96–1.04.

Field Demonstration: Interference

20190729 2500 200 $slope = 0.989 \pm 0.001$ intcpt = 1.38 ± 0.09 2000 (nqdd) EO r² = 0.95 1500 July 29 flight from Boise, ID to Northwestern forest ROZE 1000 wildfires 50 500 0 0 50 100 150 200 0 NOyO3 O3 (ppbv)

ROZE is subject to interference from UV-active species (e.g., aromatic hydrocarbons, SO₂). Figure colored by CO mixing ratio (ppbv) to indicate smoke.

Field Demonstration: remaining biases

Aug 29 flight from Salina, KS flight over KS, NE, OK tallgrass prairie fires



Eddy covariance fluxes

SARP/FIREX-AQ July 17, 2019 Pacific Ocean, Altitude = 170 m



Example spectra from a 50 km flux leg: a) Vertical wind-scalar cross covariance functions; b) Power spectra, normalized to total variance; c) Co-spectral power of 03 and H20 with vertical wind (solid) and repective ogives (dashed).

ROZE Pictures



ROZE on DC-8 rack

Top view





Instrument front panel

Thanks!

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| Reem A. Hannun ^{[0]1,2} , Andrew K. Swanson ^{1,3} , Steven A. Bailey ¹ , Thor Ilann Bourgeois ^{[0]5,6} , Jeff Peischl ^{[0]5,6} , and Thomas B. Ryerson ⁵ ¹ Atmospheric Chemistry and Dynamics Laboratory, NASA Goddard Spaceflight C ² Joint Center for Earth Systems Technology, University of Maryland Baltimore Co ³ Universities Space Research Association, Columbia, MD, USA ⁴ Earth Science Division, NASA Ames Research Center, Moffett Field, CA, USA | mas F. Hanisco ^{D1} Center, Greenbelt, MD, unty, Baltimore, MD, U | , T. Paul Bui⁴, USA JSA | |

⁵NOAA Chemical Sciences Laboratory, Boulder, CO, USA

⁶Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, CO, USA



Reem Hannun and Andrew Swanson with the ROZE breadboard prototype