Continuous year-long measurements of atmospheric HONO and NO$_2$ above a New England forest

Ben Lee$^1$, Bill Munger$^1$, Ezra Wood$^{2,3}$, Mark Zahniser$^3$ and Steve Wofsy$^1$

$^1$ Harvard University
$^2$ Umass Amherst
$^3$ Aerodyne Research, Inc.

AMS Conference on Atmospheric Biogeosciences
May 29, 2012
Daytime chemistry

R1. OH + NO + M → HONO + M
R2. HONO + OH → H₂O + NO₂
R3. HONO + hν → OH + NO
Daytime chemistry

R1. \( \text{OH} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M} \)

R2. \( \text{HONO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2 \)

R3. \( \text{HONO} + \text{hv} \rightarrow \text{OH} + \text{NO} \)

\[
\frac{d[\text{HONO}]}{dt} = k_1[\text{OH}][\text{NO}] - k_2[\text{HONO}][\text{OH}] - J_{\text{HONO}}[\text{HONO}]
\]
**Daytime chemistry**

R1. \( \text{OH} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M} \)

R2. \( \text{HONO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2 \)

R3. \( \text{HONO} + h\nu \rightarrow \text{OH} + \text{NO} \)

\[
\frac{d[HONO]}{dt} = k_1[OH][NO] - k_2[HONO][OH] - J_{HONO}[HONO]
\]

\[
[HONO]_{PSS} = \frac{k_1[OH][NO]}{J_{HONO} + k_2[OH]}
\]
**Daytime chemistry**

R1. \( \text{OH} + \text{NO} + \text{M} \rightarrow \text{HONO} + \text{M} \)

R2. \( \text{HONO} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{NO}_2 \)

R3. \( \text{HONO} + h\nu \rightarrow \text{OH} + \text{NO} \)

\[
\frac{d[HONO]}{dt} = k_1[OH][NO] - k_2[HONO][OH] - J_{HONO}[HONO]
\]

\[
[HONO]_{PSS} = \frac{k_1[OH][NO]}{J_{HONO} + k_2[OH]}
\]

[Zhou et al., 2002]

Pinnacle State Park, NY (Jul 1998)

Observed

PSS

\[ \text{HONO}, \text{ppmv} \]

\[ \text{Time, LT} \]
• “Missing” HONO source accounts for 20-40% of P(HO$_x$)

• Pathway to recycle deposited NO$_x$ back into atmosphere in reactive form
Questions

• What is the contribution of HONO production on atmospheric NO\textsubscript{x} and HO\textsubscript{x} budgets over a rural forest?

• Which environmental variables are responsible?
Goals for instrument

- Direct sampling (no wet chemistry)
- Selectivity (spectroscopic identification)
- Sensitivity (pristine environments & eddy covariance fluxes)
- Long-term deployment (cryogen-free)
Tunable Infrared Laser Differential Absorption Spectroscopy
**Tunable Infrared Laser Differential Absorption Spectroscopy**

- **A)** QC laser for HONO (1660 cm\(^{-1}\))
- **B)** QC laser for NO\(_2\) (1604 cm\(^{-1}\))
- **C)** 210-m path-length multi-pass astigmatic cell
- **D)** Detector
1-hr avg. spectra (6:30-7:30 am on 1/18/2011)

Spectra provide unambiguous identification of HONO
Sampling system

- Routine in-field tests on sampling system to ensure artifact-free measurements
- No particle filters
Sampling system

- Routine in-field tests on sampling system to ensure artifact-free measurements
- No particle filters
Quick glance by season

Winter
Spring
Summer
Autumn
Comparison to previous measurements: mixing ratio

$\Delta$ UMBS: Jul-Aug ’08 [Zhou et al. 2011]
Comparison to previous measurements: fluxes

Fluxes by relaxed eddy accumulation

[Zhou et al., 2011]
Comparison to previous measurements: fluxes

Previous rural studies infer daytime HONO flux ranging from $3.6 \times 10^{-6}$ to $59 \times 10^{-6}$ mol m$^{-2}$ h$^{-1}$

[Ren et al., 2010; Acker et al., 2006; Kleffmann et al., 2005; Zhou et al., 2002]
Daytime result

Daytime HONO production at Harvard Forest contributes negligibly to atmospheric HO$_x$ and NO$_x$ budget over all seasons