H101: Surface-Induced Oxidation of Organics in the Troposphere (SOOT)

Renyi Zhang, Don Collins, and Simon North

Department of Atmospheric Sciences and

Department of Chemistry
Texas A&M University

College Station, TX 77843

Presented at the SAC/TERC Meeting, October 23, 2008

Scientific Objectives

To assess heterogeneous chemistry on radical budget, VOC oxidation, and ozone formation in the Houston area

- **HONO Formation**
  NO_2 + Soot $\rightarrow$ HONO
  $\gamma \approx 1.1 \times 10^{-2}$ to 3.3×10^{-4}, depending on the mixing state of soot
  HNO_4 + surface $\rightarrow$ HONO
  A source for OH in the morning hours

- **N_2O_5 Hydrolysis**
  $N_2O_5 + H_2O$(aerosol) $\rightarrow 2HNO_3$
  $\gamma \approx 0.1$ to < 0.001, depending on the nitrate and organic contents
  $NO_2 + O_3 \rightarrow NO_3 + O_2$
  $NO_2 + NO_3 + M \rightarrow N_2O_5$
  NO_3 as a nighttime oxidant
  NO_3 + VOCs $\rightarrow$ Peroxides
  A source for OH on the following day

Proposed Activities

Lab Experiments:

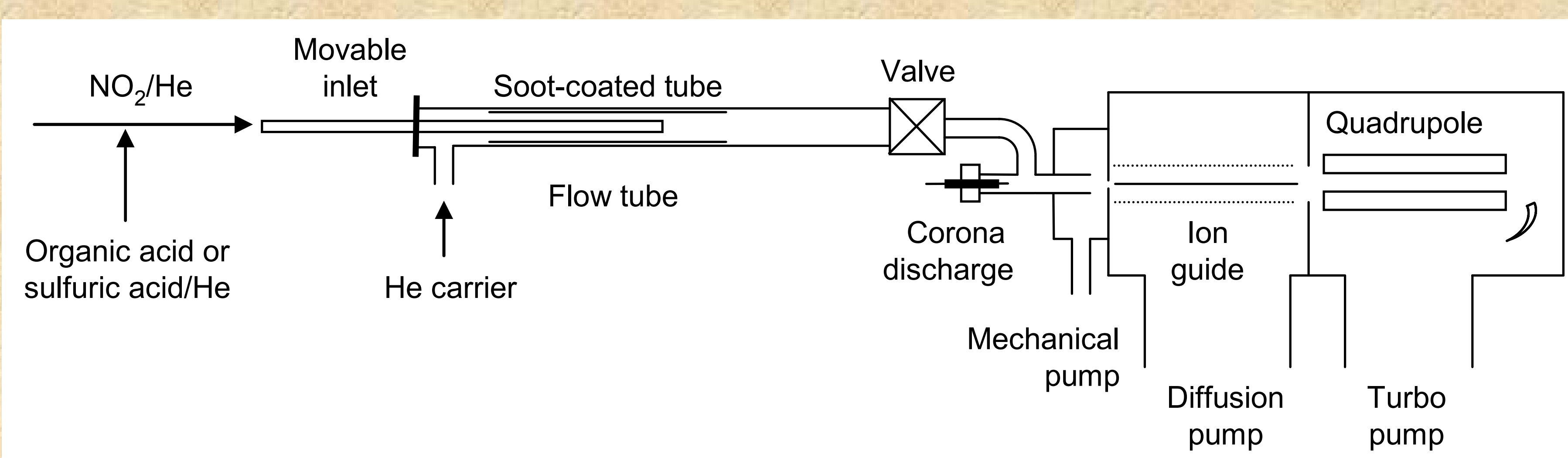
Measurements of the uptake coefficients of NO_x and HONO formation rate on fresh and aged soot with variable amounts of organics, sulfate, and nitrate

- **A fast-flow laminar flow reactor with coated soot surfaces**
- **A captured chamber with sub-micrometer soot particles**

Field Campaign:

Simultaneous measurements of key nitrogen compounds (HONO, HNO_3, HNO_4, N_2O_5, and NO_3) and aerosols during a one-month period in 2009 at the University of Houston Moody Tower

Heterogeneous Reaction of NO_2 and HONO Formation on Soot Using a Fast-Flow Reactor

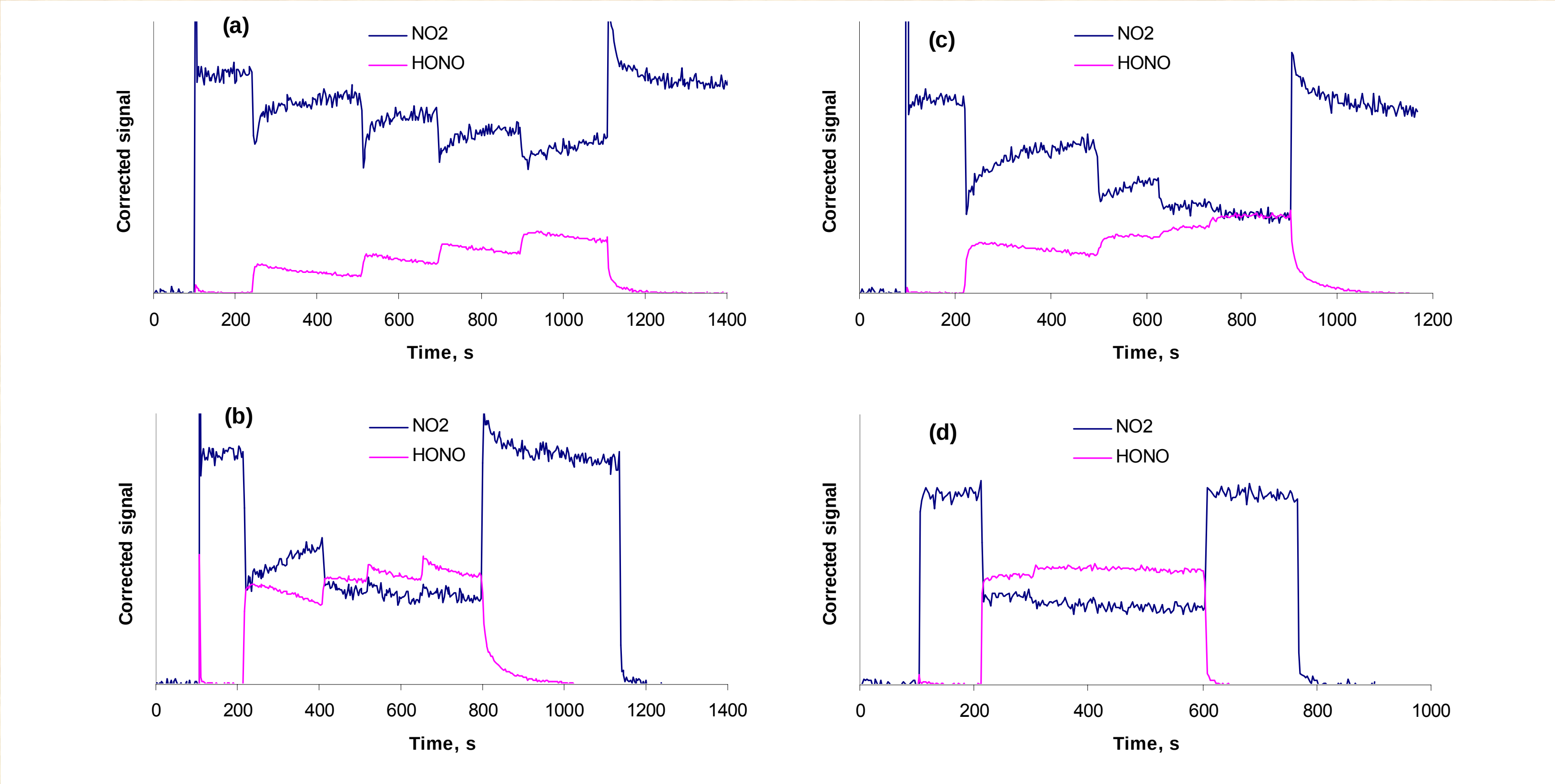


NO_2 Uptake and HONO Formation on Kerosene Soot

Activated **Unactivated**

Unheated

Heated

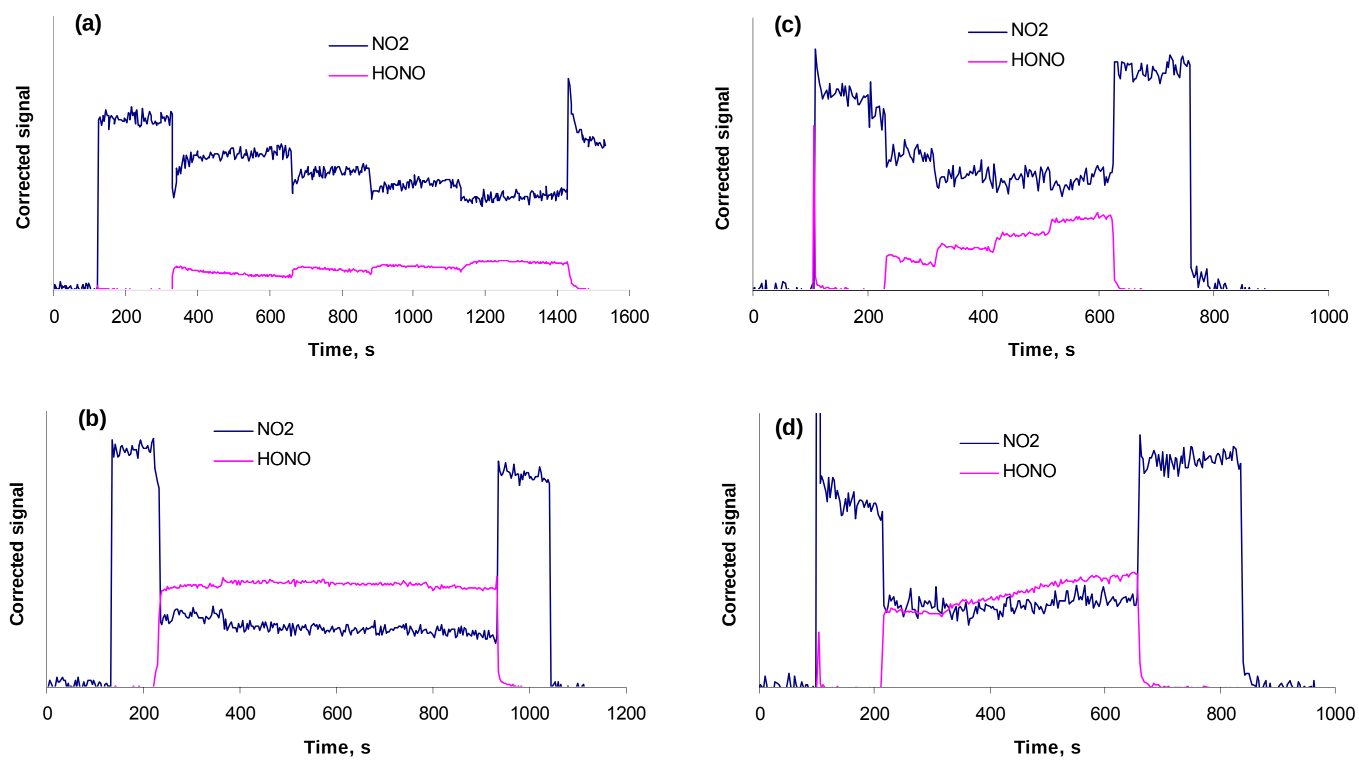


NO_2 Uptake and HONO Formation on Propane Soot

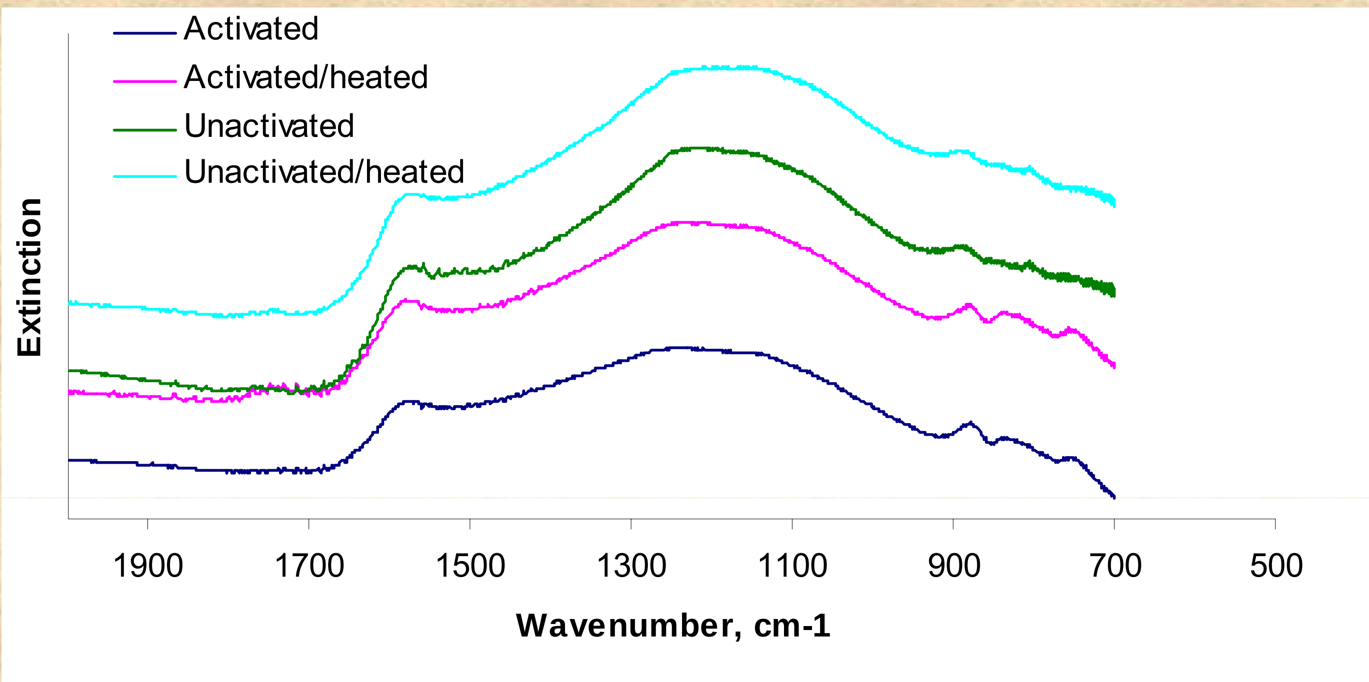
Activated | **Unactivated**

Unheated

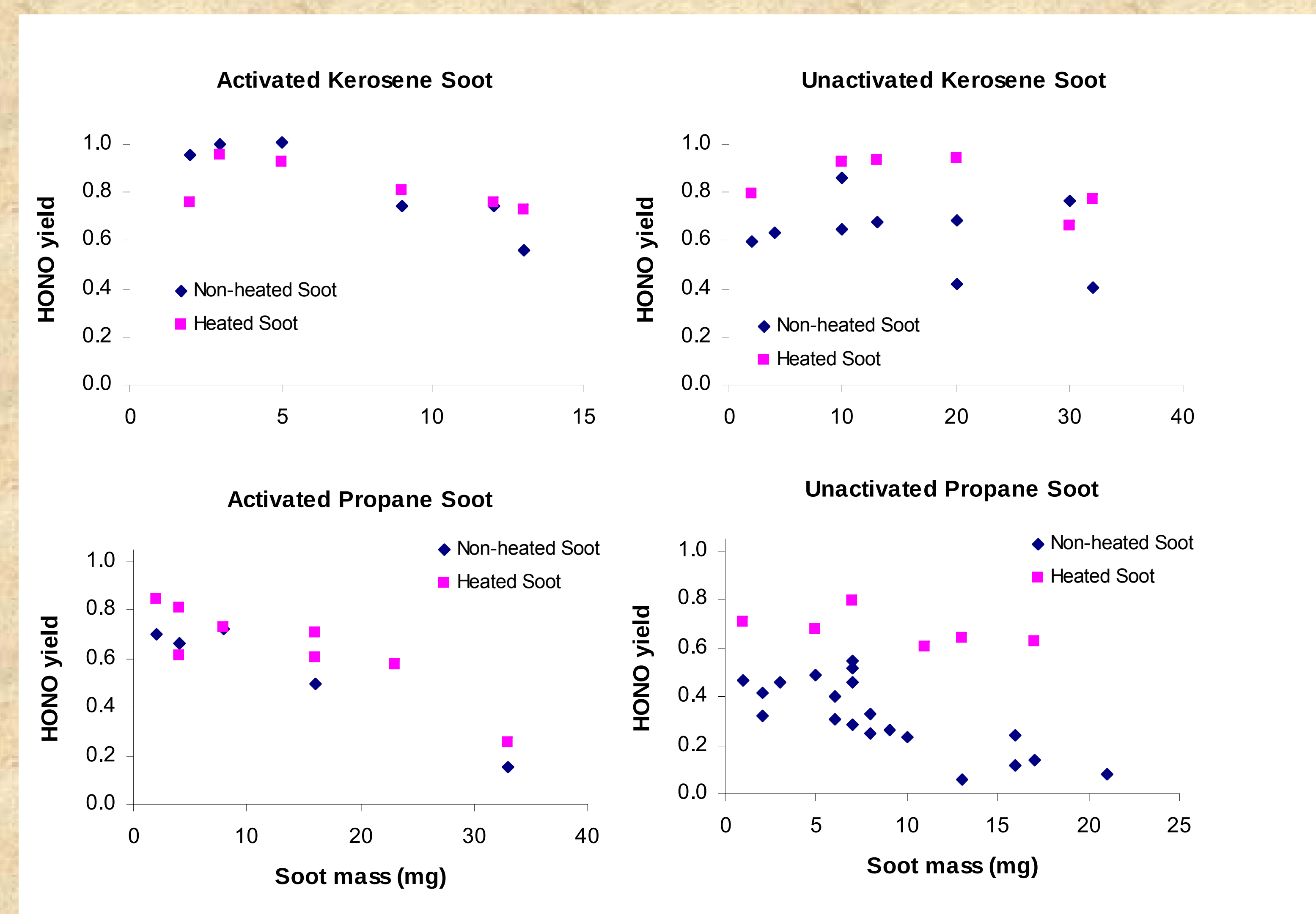
Heated



FT-IR Spectra of Various Soot Surfaces

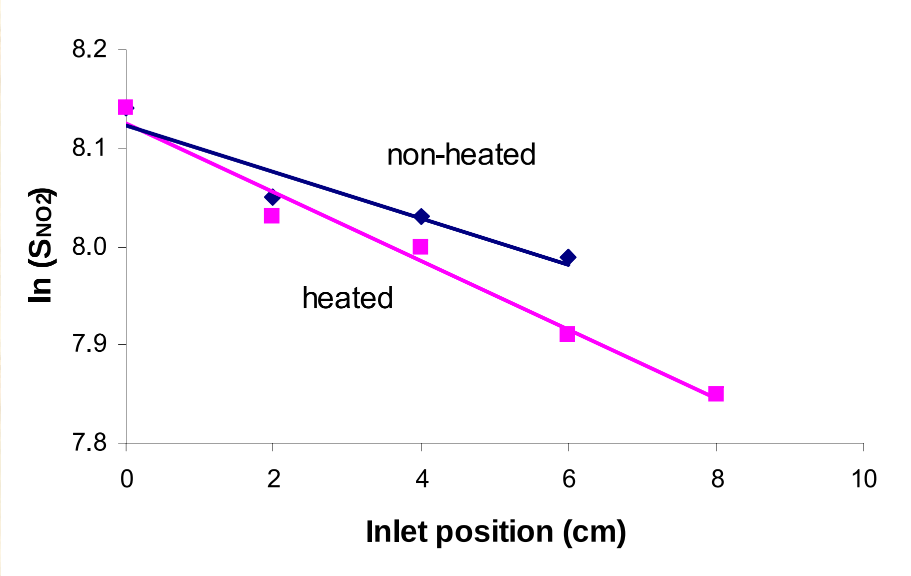


HONO Formation Yield on Propane and Kerosene Soot



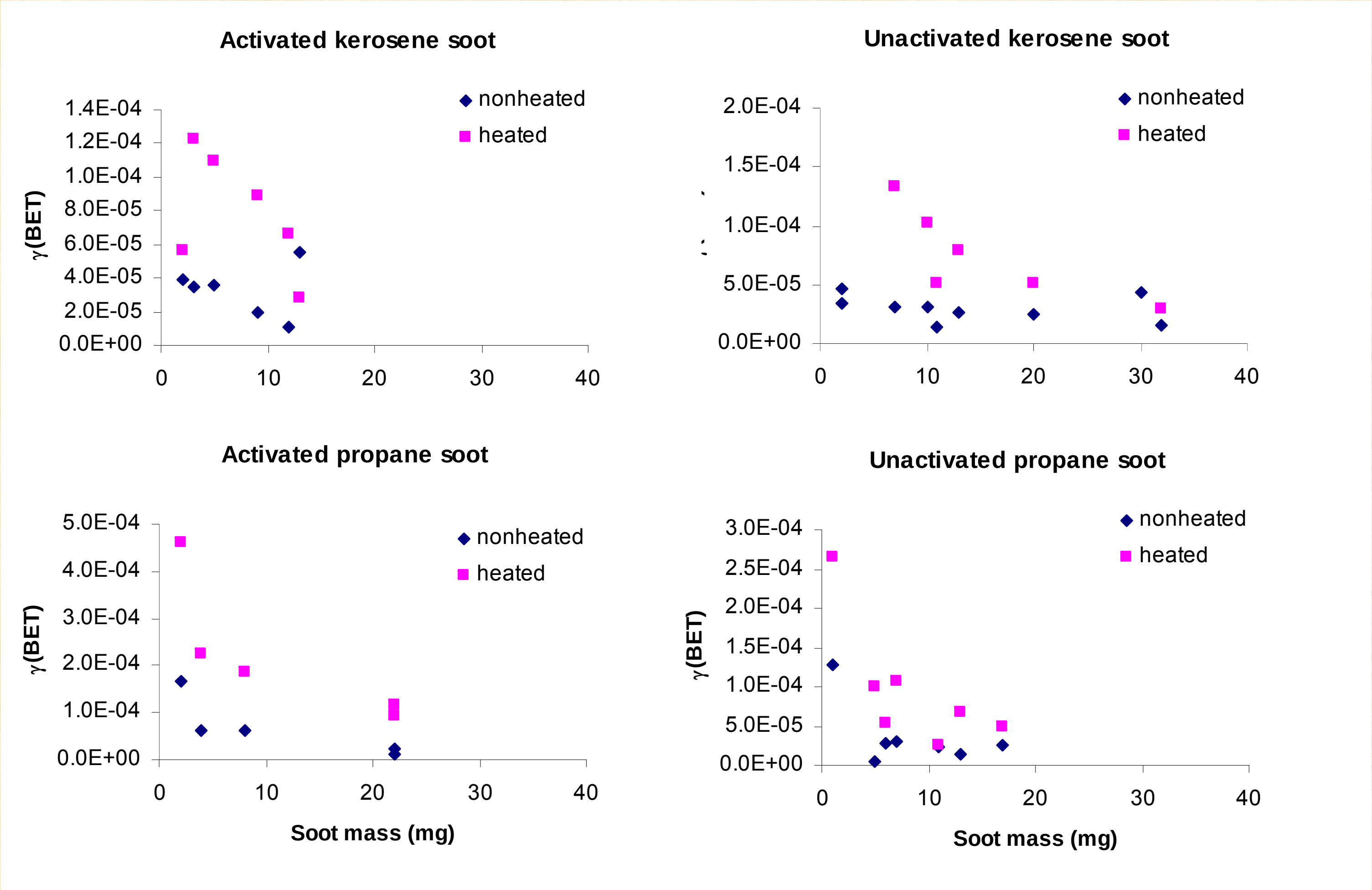
NO_2 Uptake Kinetics on Propane and Kerosene Soot

$$\gamma = \frac{2rk_w}{\omega}\frac{A_{geo}}{A_{BET}}$$

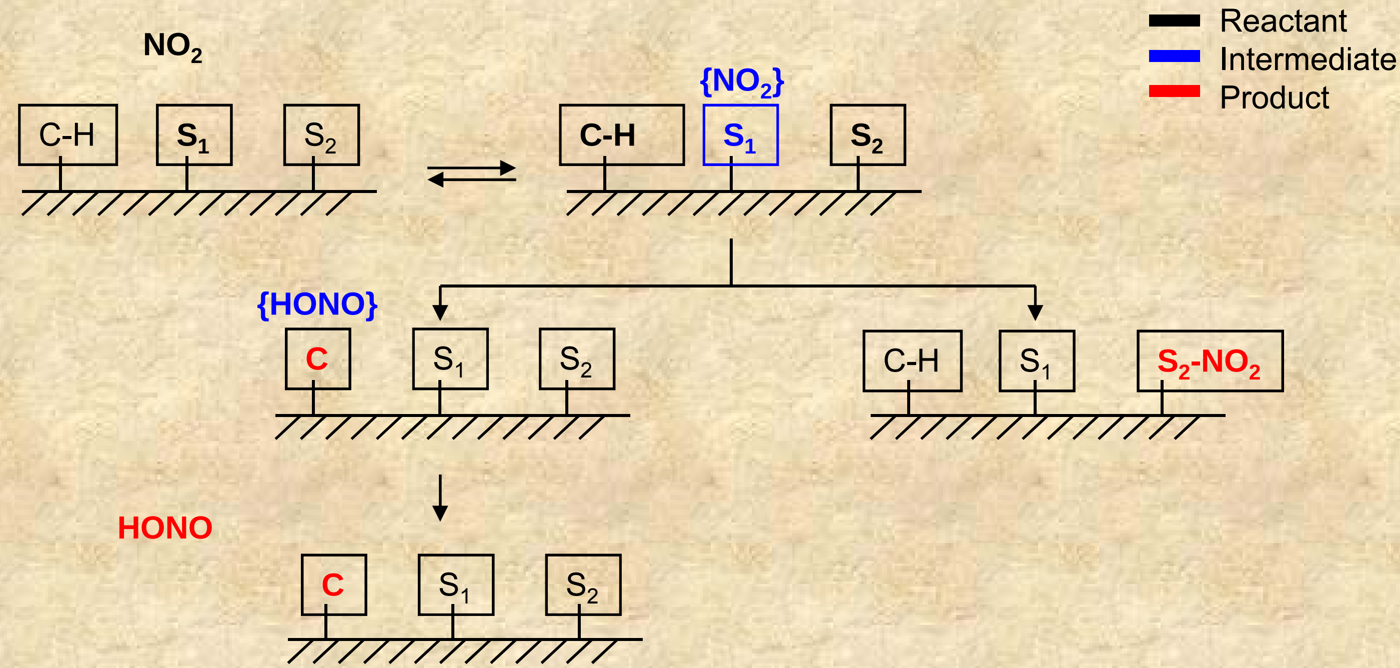


Fuel	BET specific surface area, m^2 g^{-1}	
	Unactivated	Activated
Propane	150	75
Kerosene	105	75

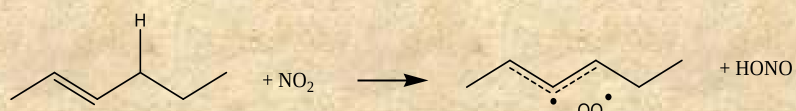
NO_2 Uptake Coefficient on Propane and Kerosene Soot



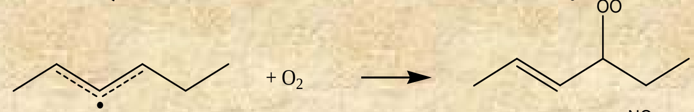
NO_2 Uptake Mechanism



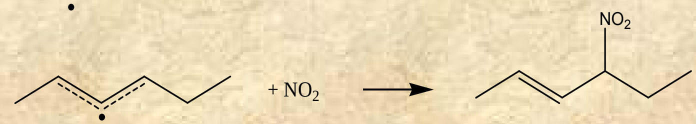
Low NO_2 concentration:



In the presence of O_2:

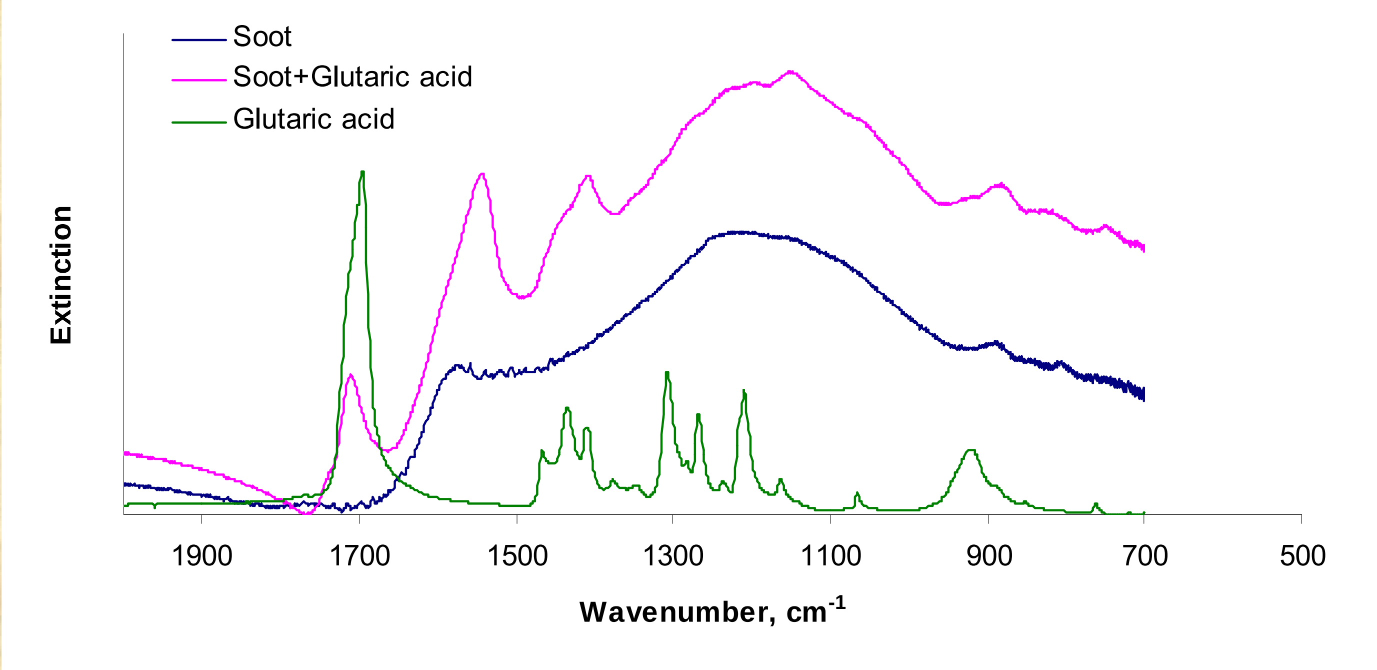


High NO_2 concentration:



***W.A. Pryor and J.W. Lightsey, Science* (1981)**

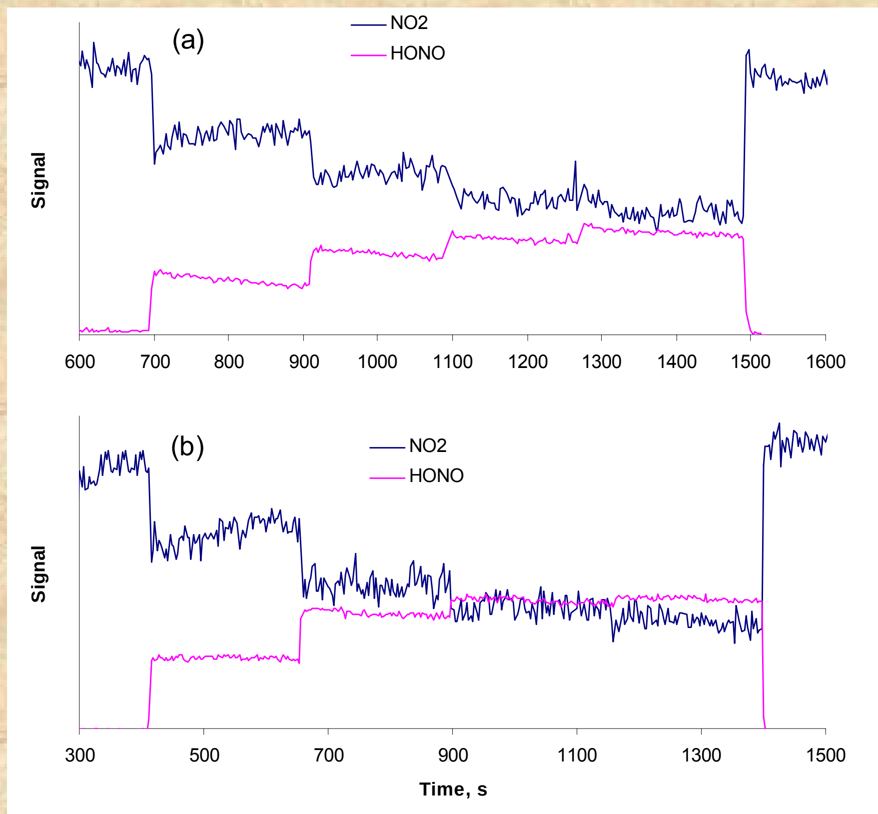
Coating of Soot by Organic and Sulfuric Acids

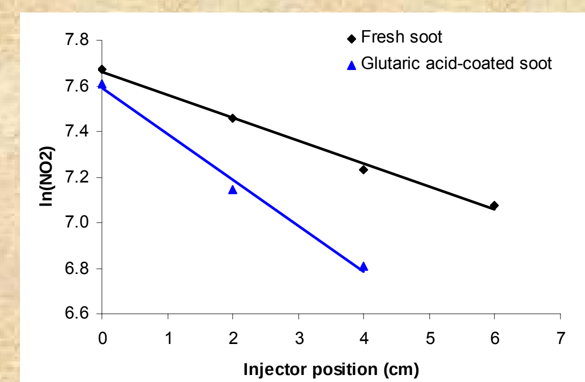


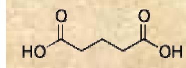
Effects of Coating of by Organic and Sulfuric Acids on NO_2 Uptake and HONO formation on Soot

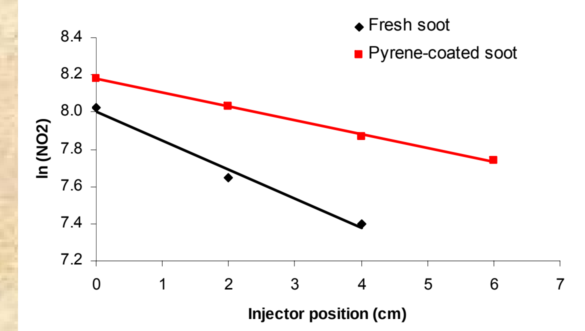
Uncoated

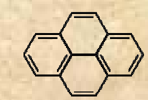
Coated











Chamber status and plans

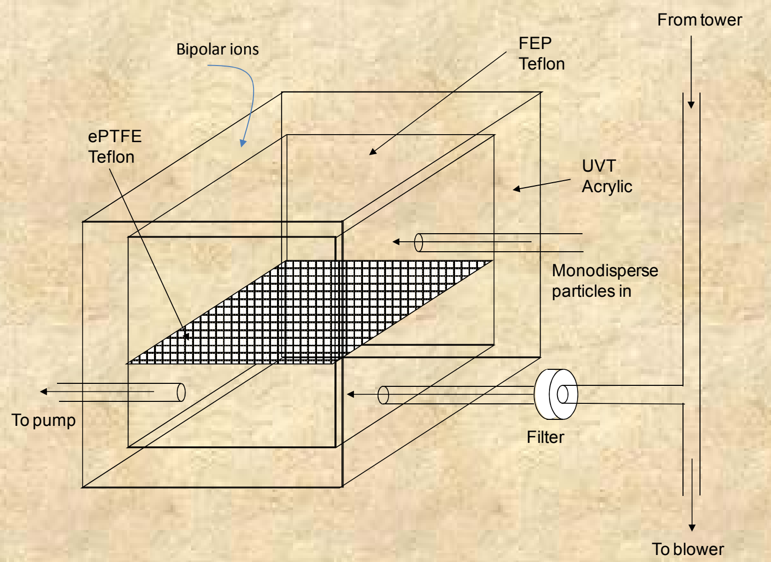
- Prepared and tested three identical chambers

- Refined testing hardware and software to facilitate full automation

- Completed initial tests with monodisperse and polydisperse soot aerosols

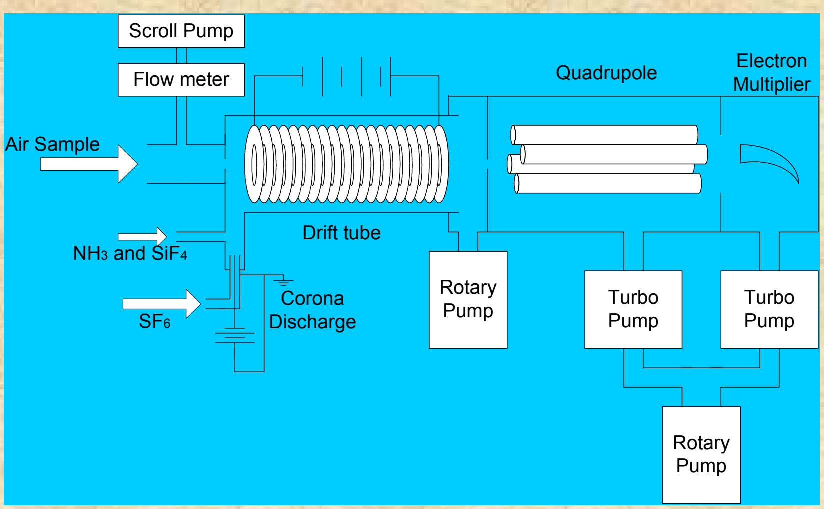
- Completed preliminary test designed to measure HONO formation inside chambers filled with soot aerosol and flushed with ambient air

- A range of additional experiments are planned prior to the field campaign



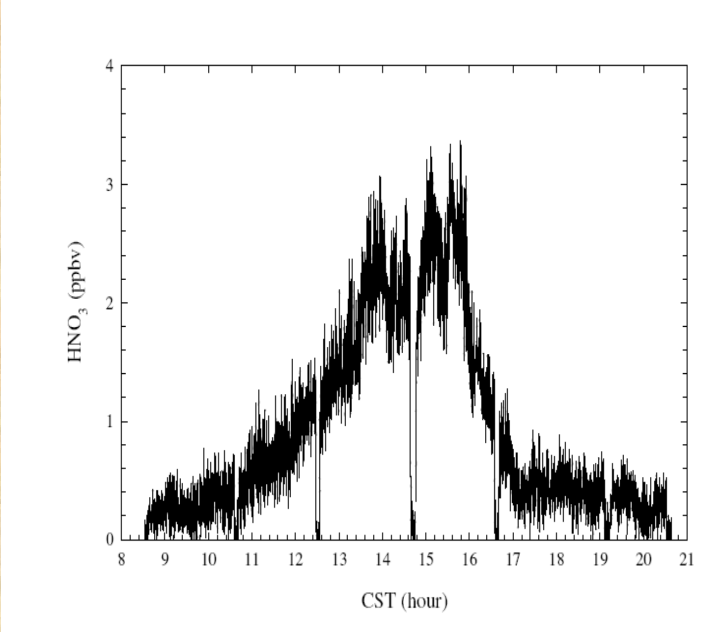
Preparation for the Proposed Field Studies

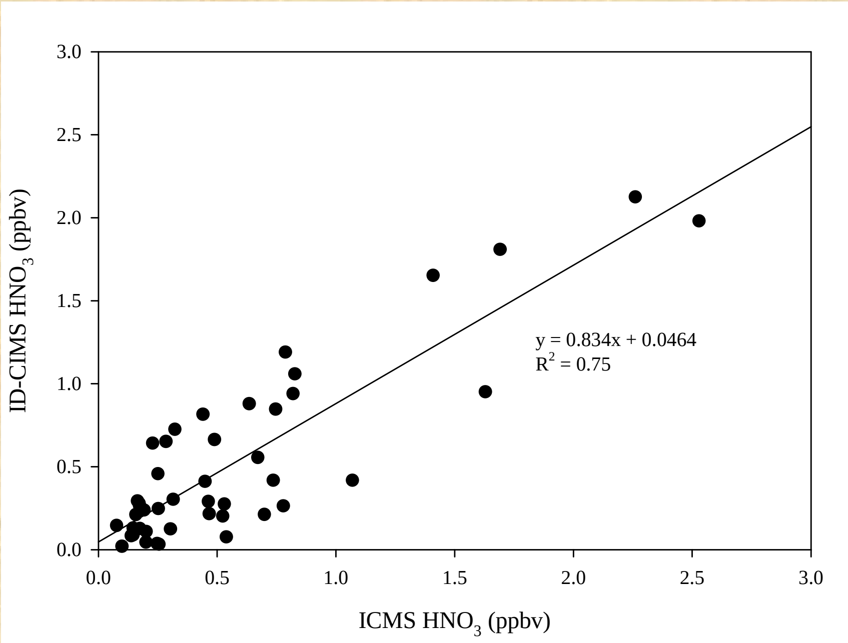
- N_2O_5 and NO_3 by cavity ring down spectroscopy (CRDS)
- HONO, HNO_3, and HNO_4 by ID-CIMS
- Soot aerosol content and mixing state by TDMA – aerosol particle mass (APM) analyzer
- Aerosol optical properties by CRDS for extinction and a nephelometer for scattering
- Aerosol size, distribution, and hygroscopicity by tandem differential mobility analyzer (TDMA)
- A captured-air chamber for controlled heterogeneous HONO formation
- Model simulations of heterogeneous chemistry on radical budget, VOC oxidation, and ozone formation using a constrained box model



ID-CIMS for HNO_3

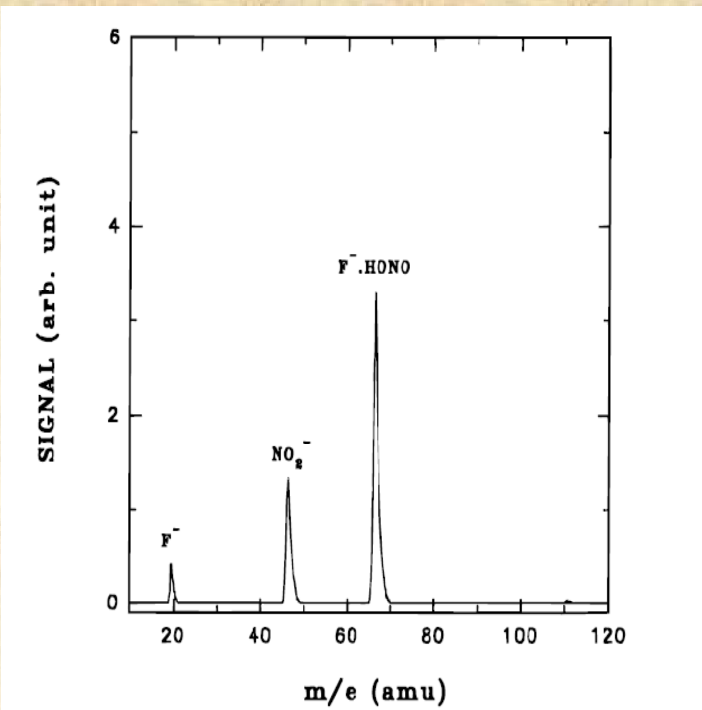
$SF_6 + e^- \rightarrow SF_6^-$
$SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5$
$SiF_5^- + HNO_3 \rightarrow SiF_5^-HNO_3$ adduct, k_1
$[SiF_5^-\cdot HNO_3] = k_1 [SiF_5^-] \Delta t [HNO_3]$

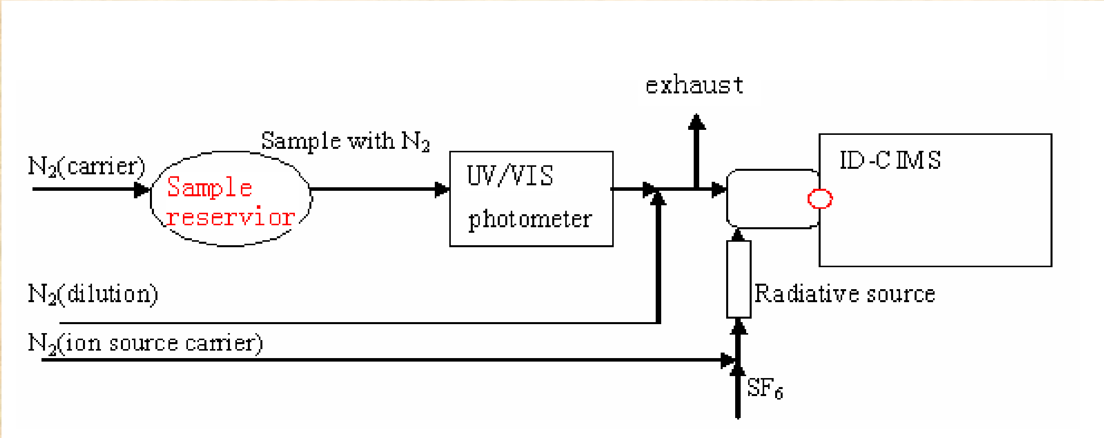


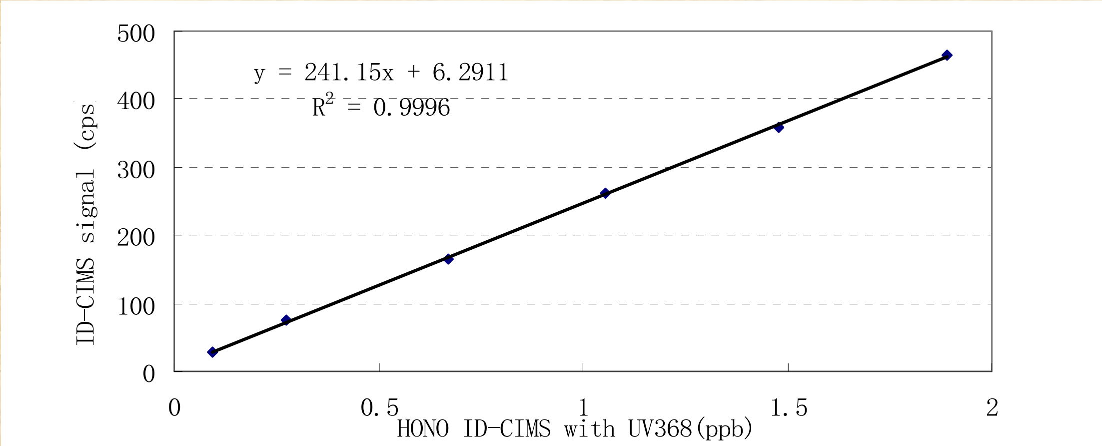


J. Zheng et al., Measurements of HNO_3 and N_2O_5 using ion drift - chemical ionization mass spectrometry during the MCMA - 2006 campaign, *Atmos. Chem. Phys.*, in press.

Measurements of HONO by ID-CIMS



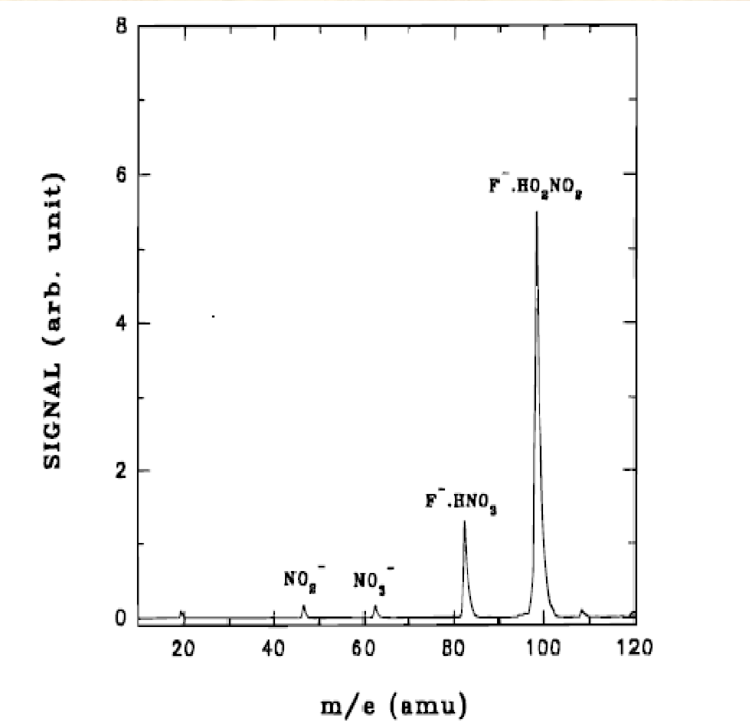


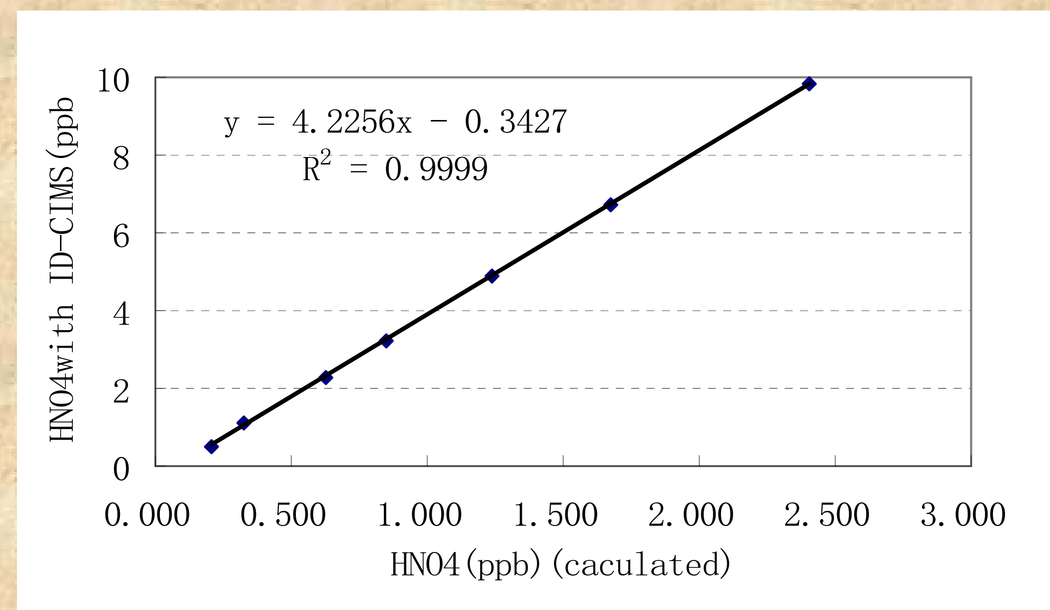


$HONO + SF_6^- \rightarrow HONO{\cdot}F^- + SF_5$

Sensitivity of 200-300 cps/ppb and a detection limit of 10-20ppt for a 1 s integration time

Measurements of HNO_4 by ID-CIMS





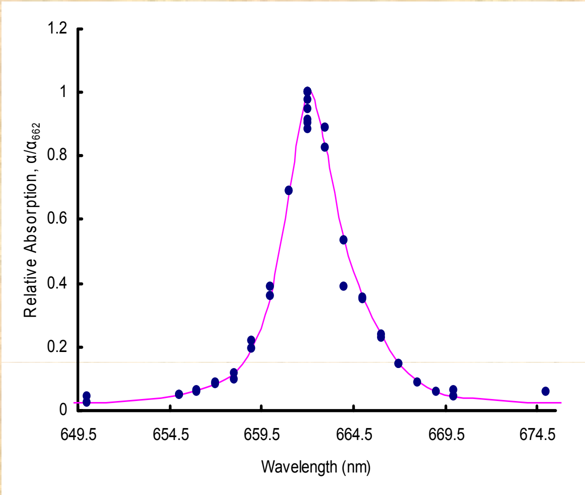
$HNO_4 + SF_6^- \rightarrow HNO_4 \cdot F^- + SF_5$
Sensitivity of 150-200 cps/ppb and a detection limit of 10-20ppt for a 1 s integration time

NO_3/N_2O_5 by Cavity Ring-Down Spectrometer (CRDS)

Simultaneous measurements of NO_3 and N_2O_5

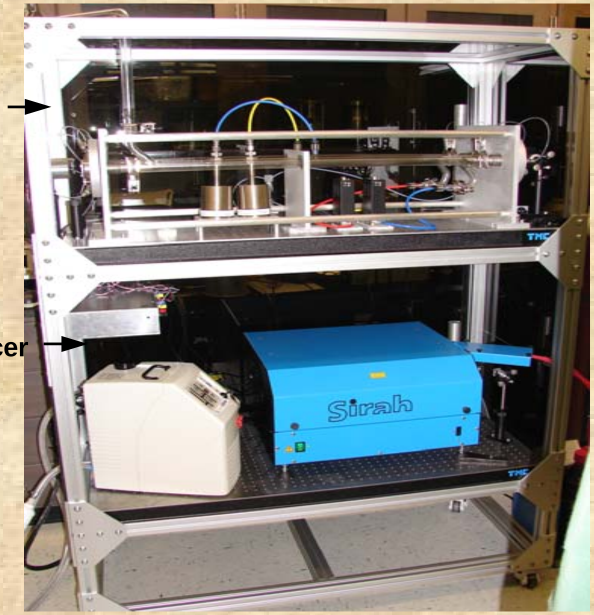
$$N_2O_5 + M \rightarrow NO_3 + NO_2 + M$$

Sensitivity on the order of 1 ppt for short integration times



Gas inlet

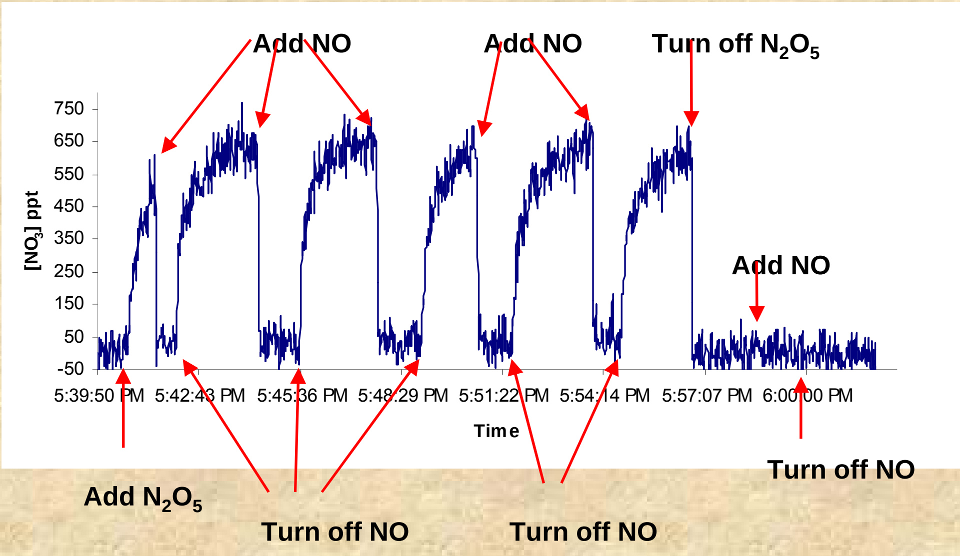
Transducer controls



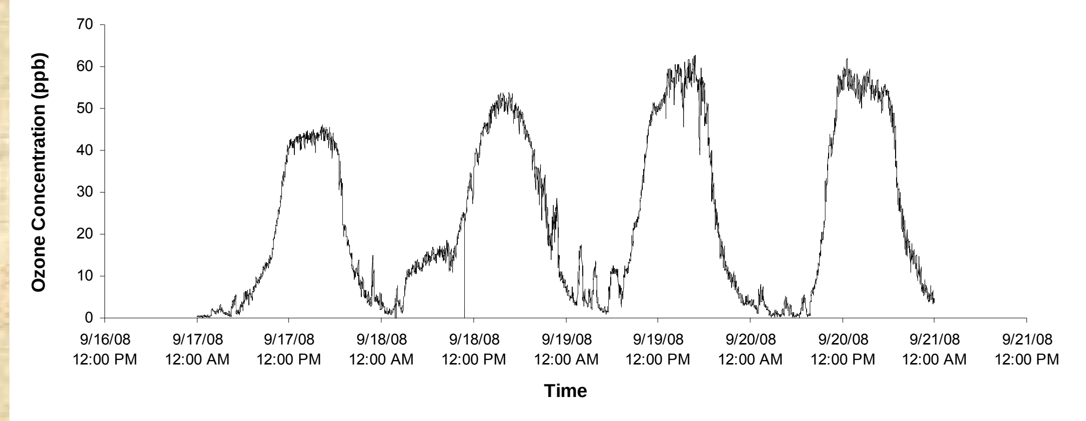
NO_3/N_2O_5 Dual Cavity

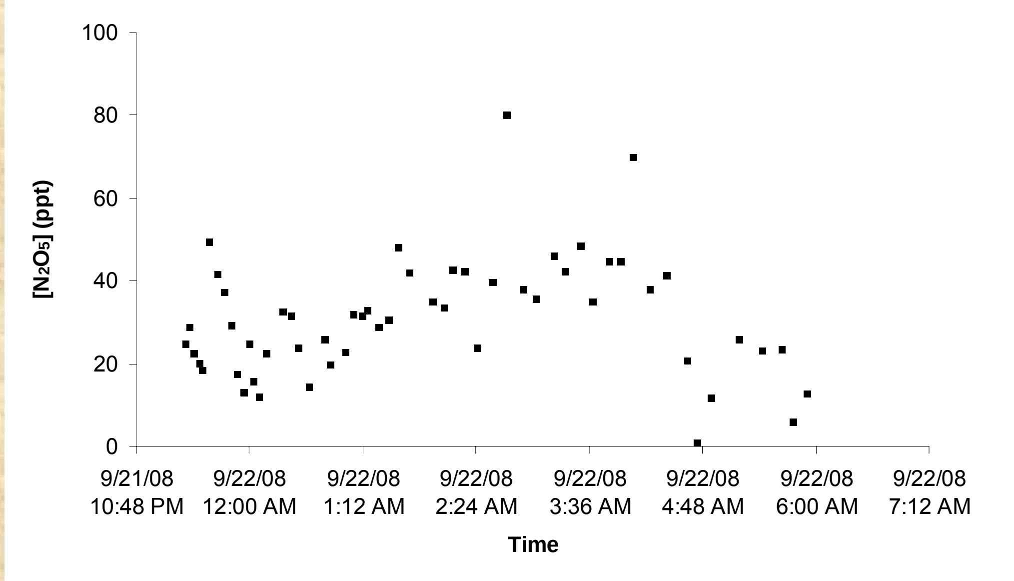
Pulsed Dye Laser System

6 mJ/pulse, 662 nm, 8 ns



Ambient N_2O_5 Measurements in College Station

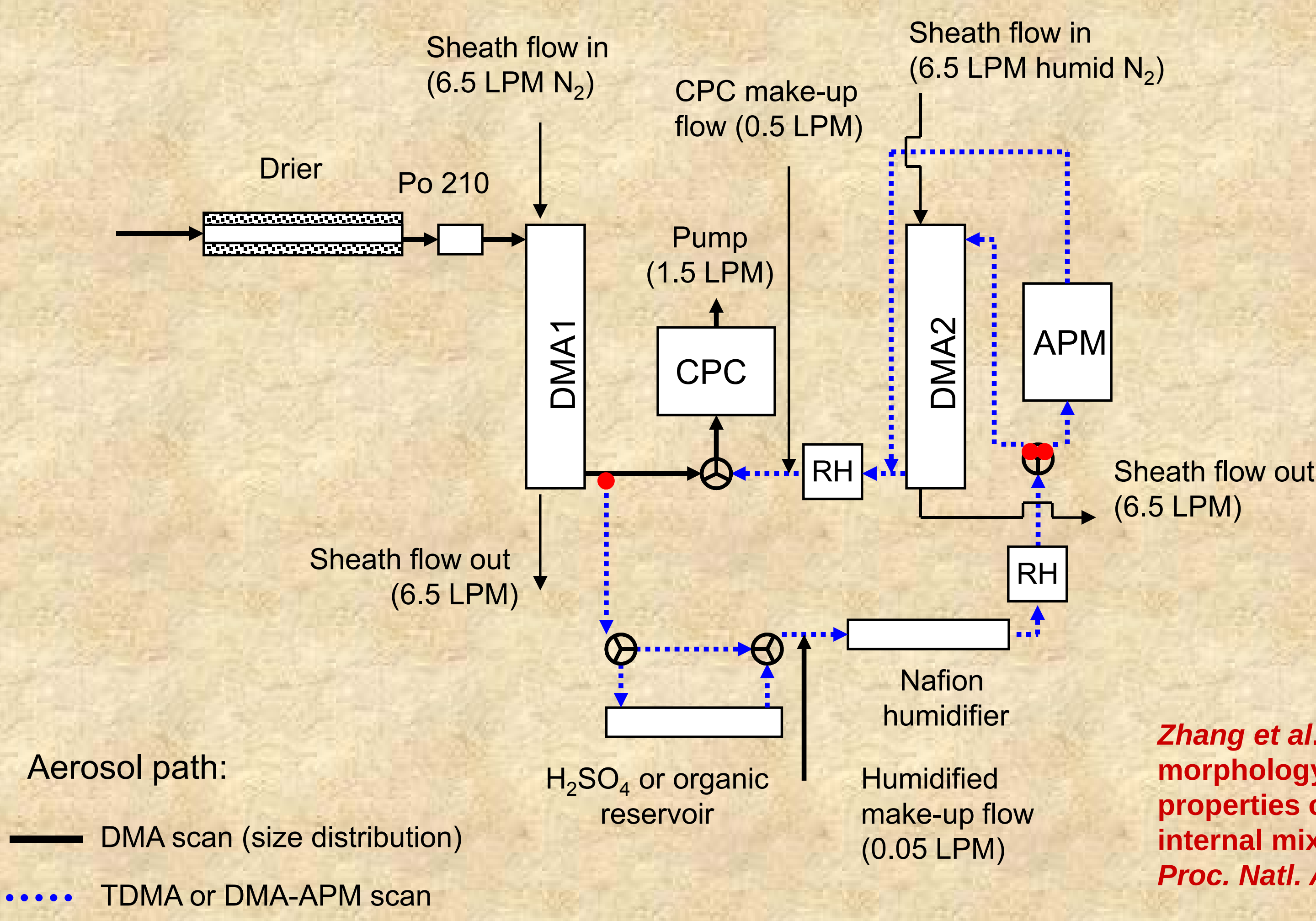




TDMA/DMA-APM system

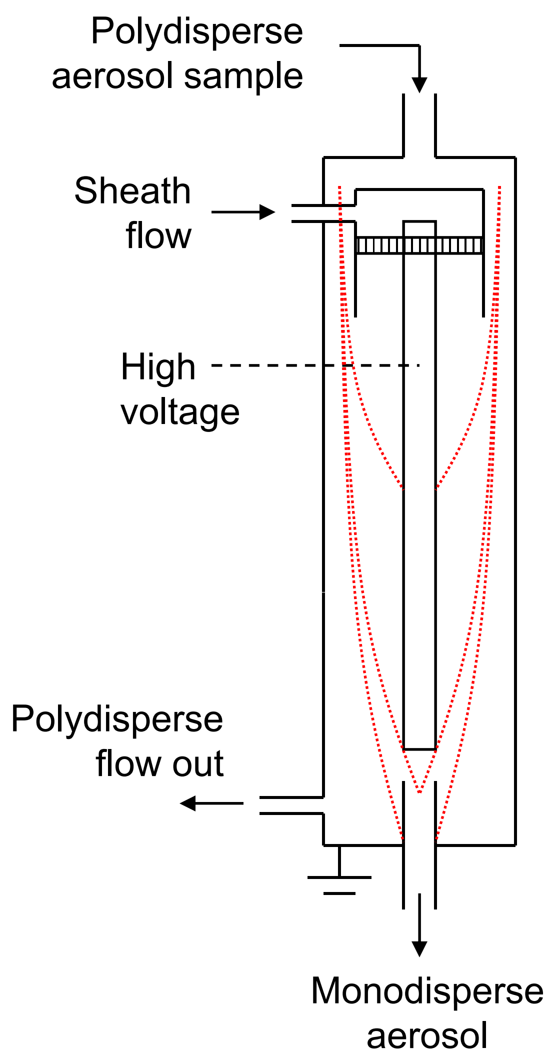
Operation modes:

- **single DMA (scanning mobility particle sizer)**
- **DMA - DMA**
- **DMA - APM**

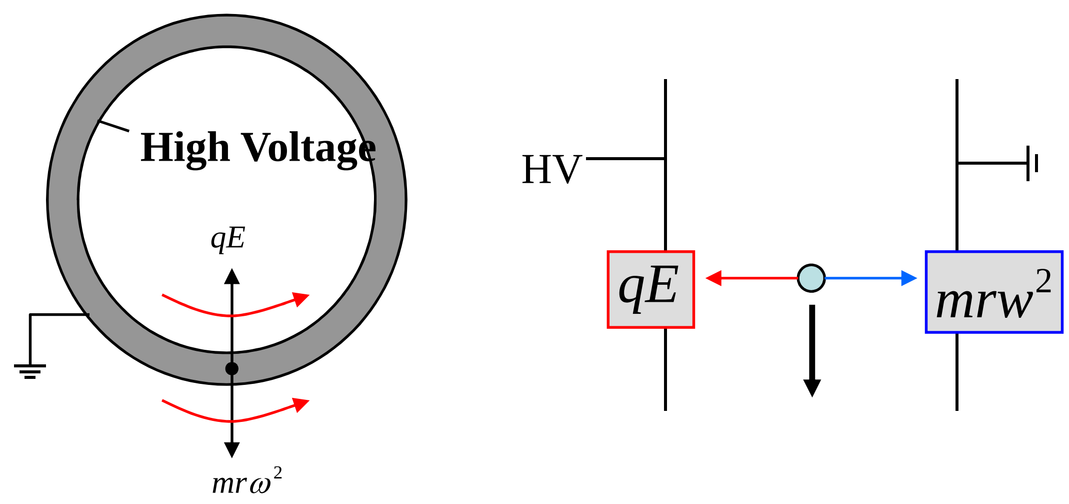


***Zhang et al.*, Variability in morphology, hygroscopic and optical properties of soot aerosols during internal mixing in the atmosphere, *Proc. Natl. Acad. Sci. USA* (2008)**

Differential Mobility Analyzer (DMA)



Aerosol Particle Mass (APM) Analyzer



DMA

- **Particles of a certain electrical mobility can penetrate through the DMA for the fixed sheath to sample flow ratio and voltage**

$$Z_p = \frac{neC}{3\pi\mu D_p}$$

APM

- **Particles of a certain mass can penetrate through the APM for the fixed rotational speed and voltage**
- **Electrostatic force = Centrifugal force**

$$mr\omega^2 = \frac{\pi d_{ve}^3}{6}\rho_{true} r\omega^2 = neE_{APM}$$

Effective Density and Fractal Dimension of Soot

- **Effective density of soot calculated from the mass (DMA-APM) and mobility (DMA-DMA) measurements**

$$\rho_{eff} = \frac{m}{V} = \frac{6m}{d_B^3 \pi}$$

- **Fractal dimension, D_f, indicates how completely a fractal appears to fill space**

$$m \propto d_B^{Df}$$

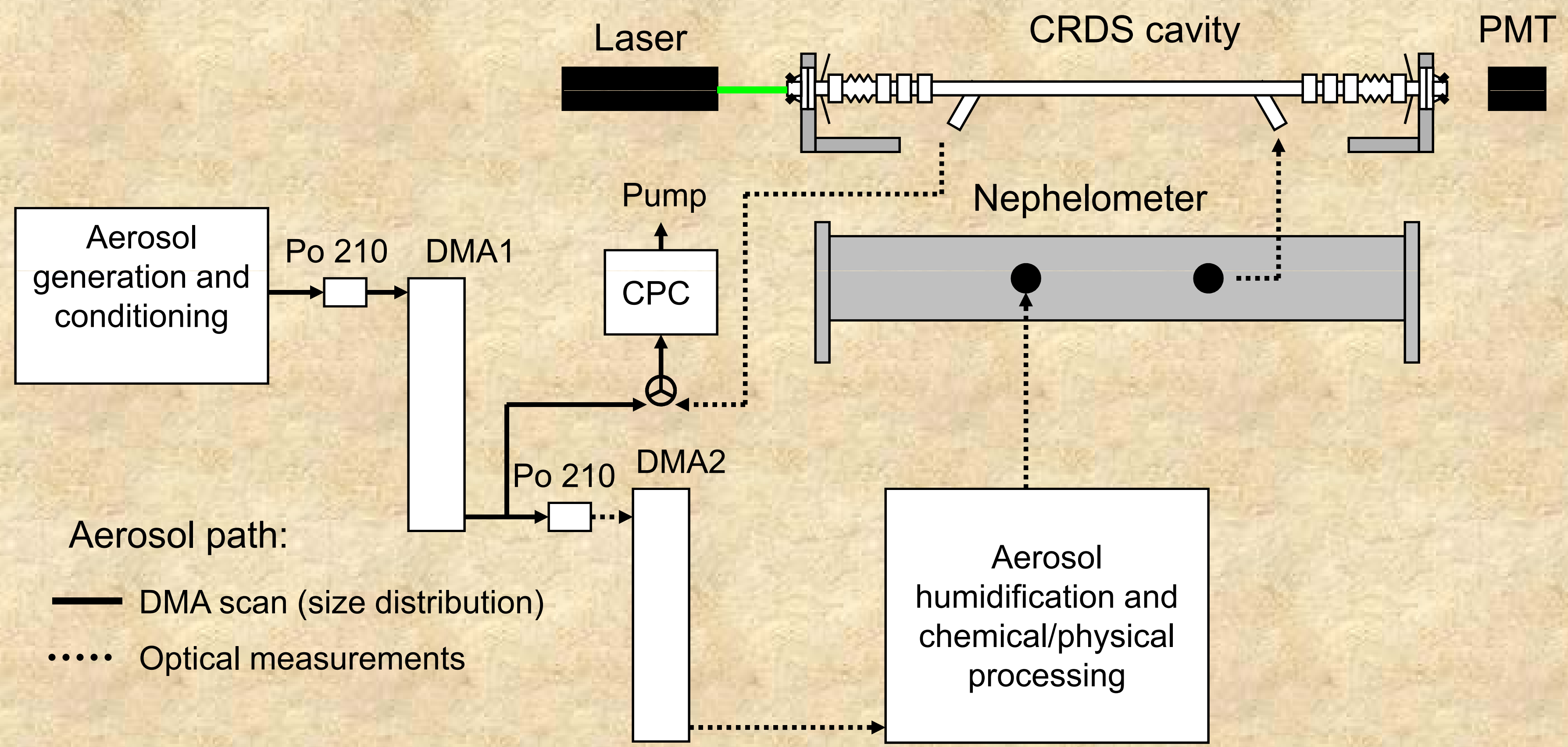
$$\rho_{eff} \propto d_B^{Df-3}$$

(d_B is mobility diameter)

- **Fractal dimension of a plane is 2**
  a solid sphere is 3

Optical Properties by DMA-DMA/Nephelometer/CRDS

- **DMA-DMA system, CRDS, nephelometer, and connecting tubing kept at a constant temperature**
- **Relative humidities in the CRDS and nephelometer within 1%**



Instrumentation List

Instrument	Availability	PI
CRDS for N_2O_5 and NO_3	Yes	North
PTR-MS and PTR-MS/MS for VOCs	Yes	Zhang
ID-CIMS for HONO, HNO_3 and HNO_4	Yes	Zhang
TDMA-APM for aerosol size and mass	Yes	Zhang
CRDS for aerosol extinction	Yes	Zhang
Nephelometer for aerosol scattering	Yes	Zhang
TDMA for aerosol size and hygroscopicity	Yes	Collins
Captured air chamber (ACES)	Yes	Collins