Surface-induced Oxidation of Organics in the Troposphere (SOOT)

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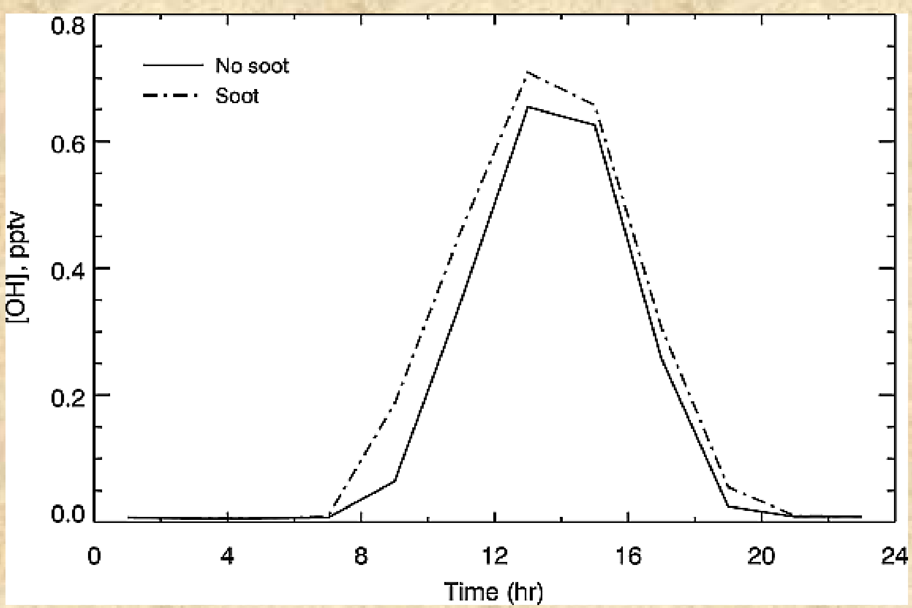
Scientific Objectives

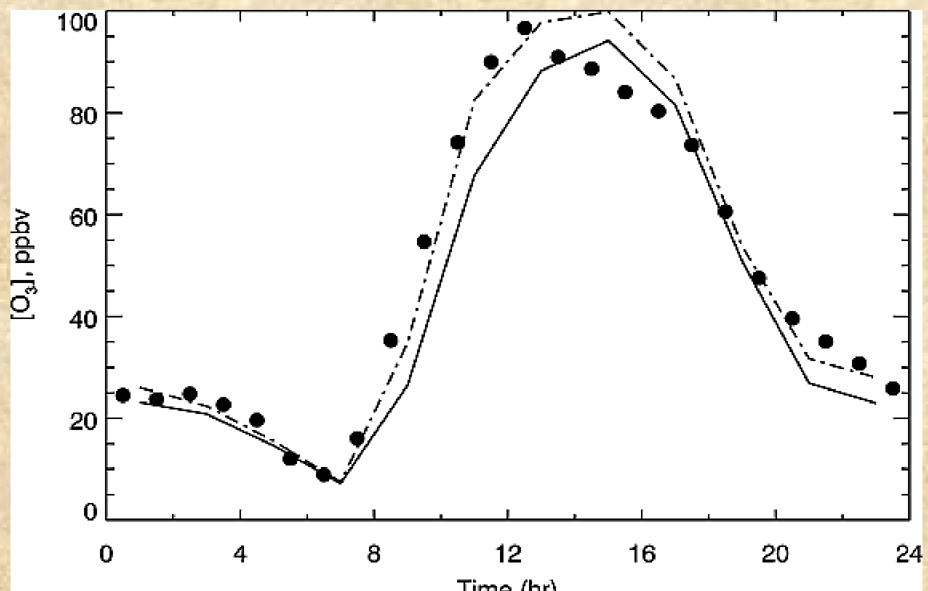
To assess heterogeneous chemistry on radical budget, VOC oxidation, and ozone formation in the Houston area

- **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

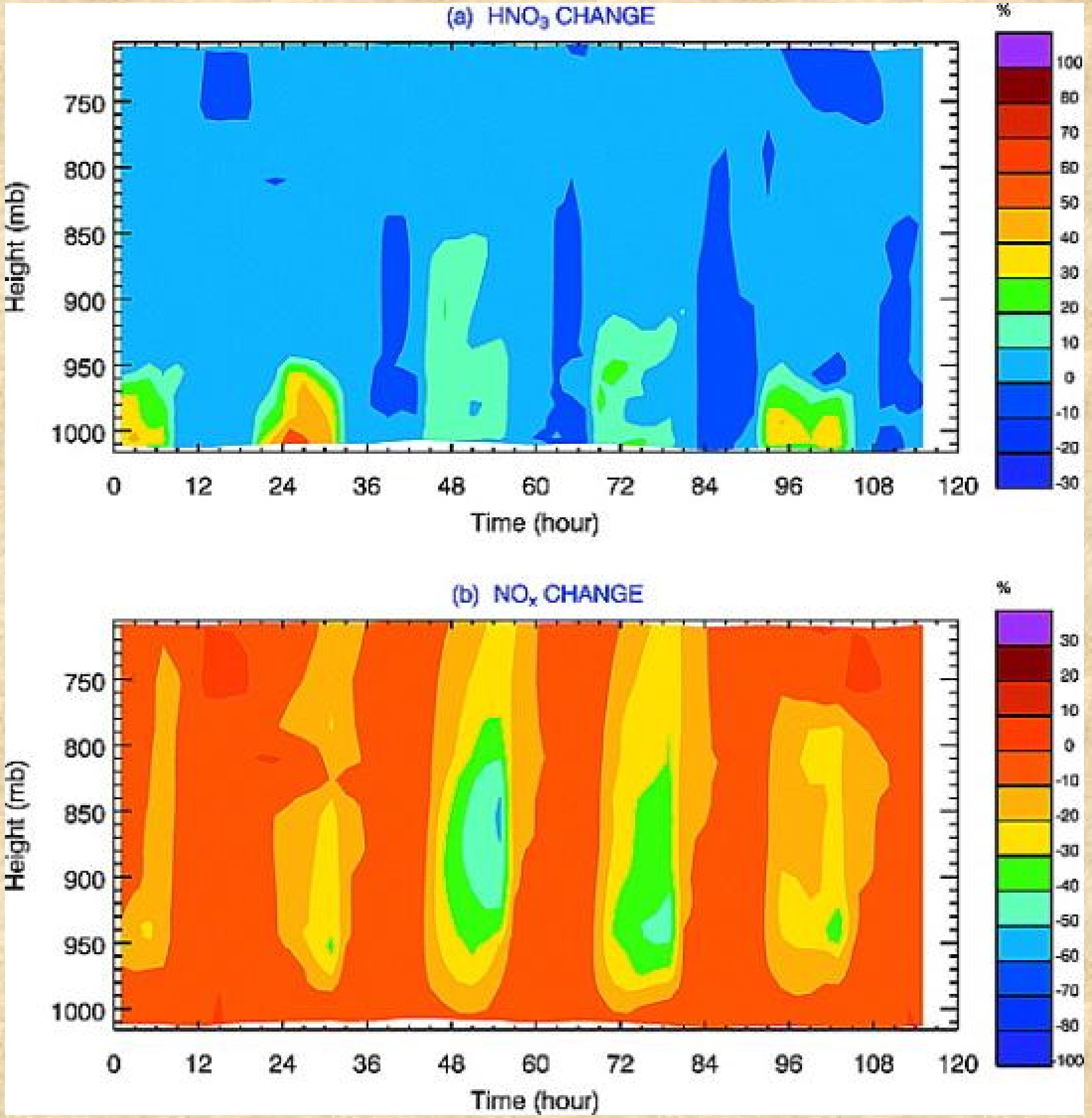
- **N_2O_5 Hydrolysis**
  $N_2O_5 + H_2O$(aerosol) $\rightarrow 2HNO_3$
  $\gamma \approx 0.1$ to < 0.001, depending on the nitrate and organic contents
  $NO_2 + O_3 \rightarrow NO_3 + O_2$
  $NO_2 + NO_3 + M \rightarrow N_2O_5$
  NO_3 as a nighttime oxidant
  NO_3 + VOCs $\rightarrow$ Peroxides
  A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

Effects of NO_2 + Soot → HONO (*Lei et al., JGR*, 2004)





Effects of $N_2O_5 + H_2O$(aerosol) $\rightarrow$ HNO_3 (*Lei et al., JGR*, 2004)



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

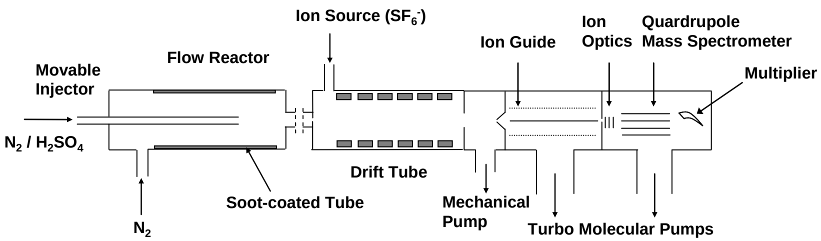
- **A fast-flow laminar flow reactor with coated soot surfaces**
- **A captured chamber with sub-micrometer soot particles**

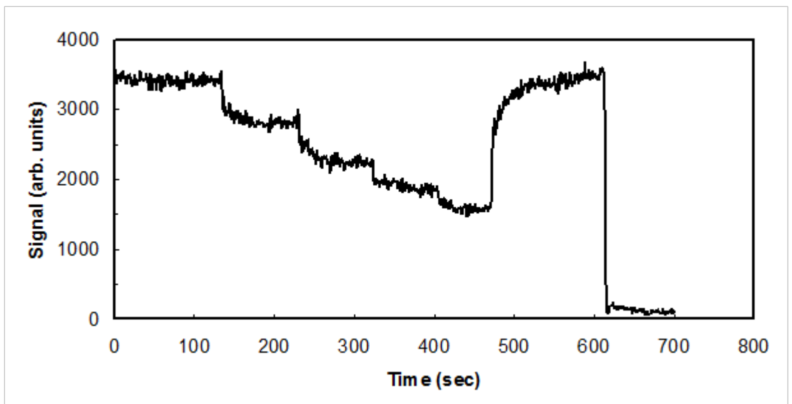
Field Campaign:

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 2008/2009 at the University of Houston's Moody Tower or from an upper floor of the Williams Tower

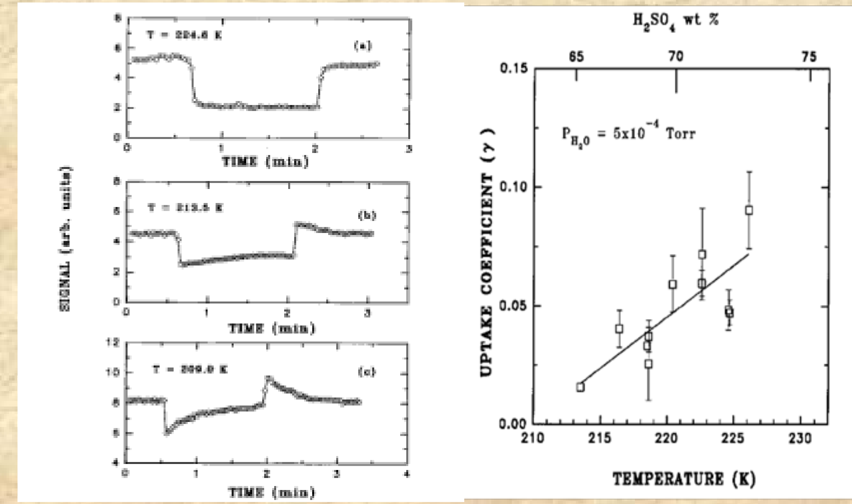
Heterogeneous HONO Formation Using a Fast Flow Reactor

Heterogeneous uptake on soot films

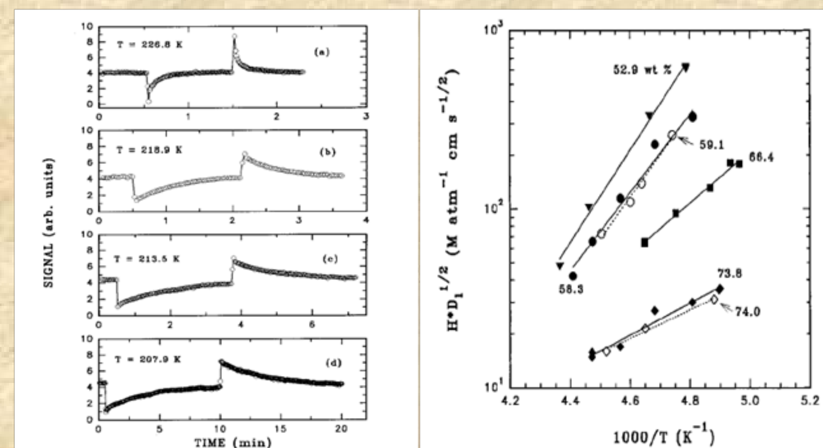




Zhang and Zhang, Laboratory investigation of heterogeneous interaction of sulfuric acid with soot, *Environ. Sci. Technol.* 39, 5722 (2005).

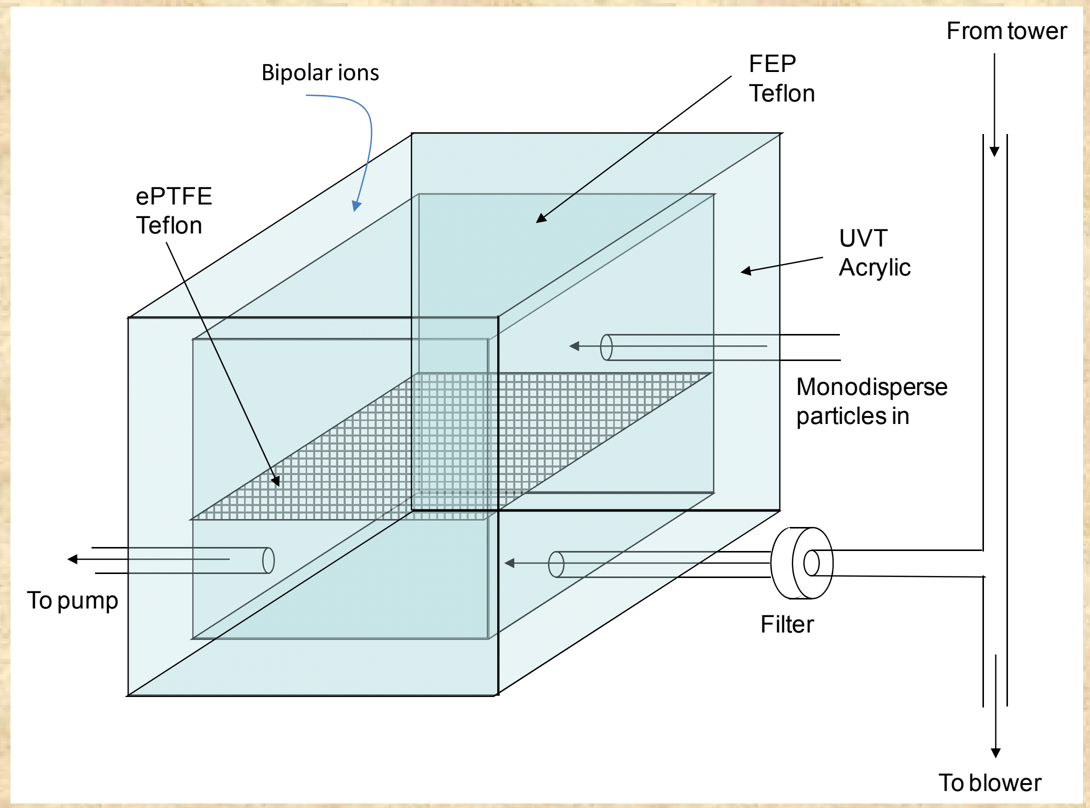


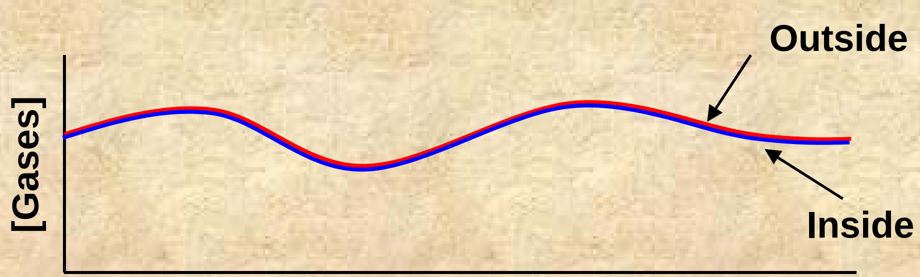
Zhang et al., Heterogeneous chemistry of HONO on liquid sulfuric acid: A new mechanism of chlorine activation on stratospheric sulfate aerosols, *J. Phys. Chem.* 100, 339 (1996).

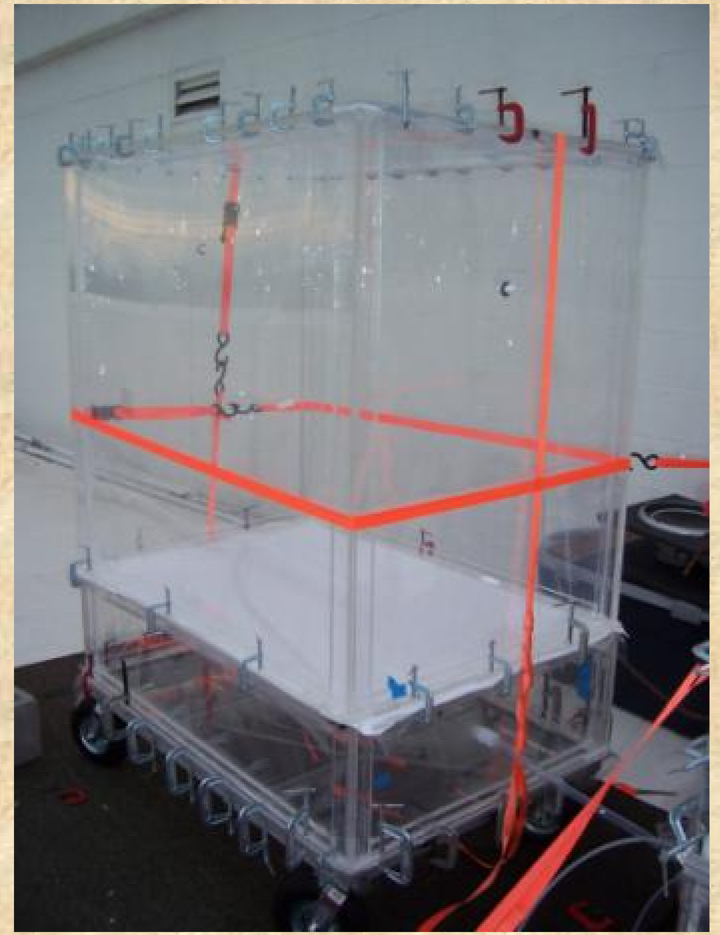


Zhang et al., Heterogeneous chemistry of HO_2NO_2 on liquid sulfuric acid, *J. Phys. Chem.* 101, 3324 (1997).

Atmospheric Chambers for Evolution Studies (ACES)



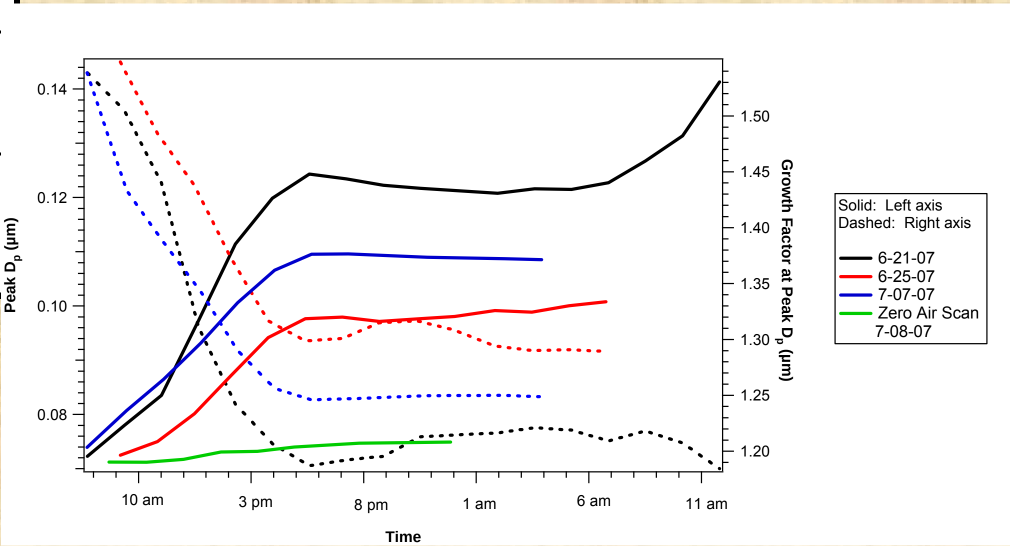




Gas Penetration Efficiency Across PTFE Membrane

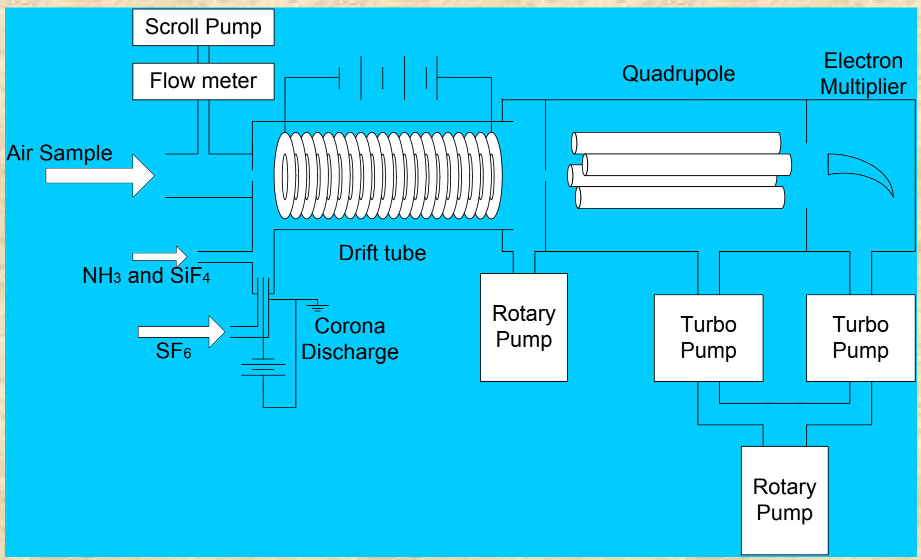
Compound Analyzed	Instruments	Penetration Efficiency
ozone	O_3 Analyzer	~92%
ethanol	PTR-MS	>99%
acetic acid	PTR-MS	>99%
toluene	PTR-MS	>99%
nitric oxide	NO_x Analyzer	>99%
sulfur dioxide	SO_2 Analyzer	>99%

Particle Growth and Hygroscopic Growth Factor



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



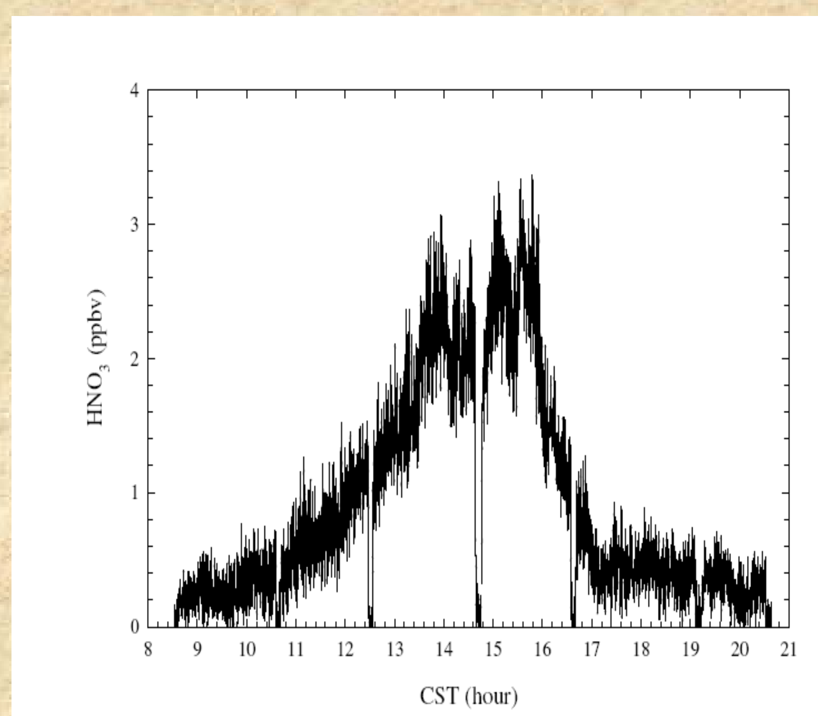
ID-CIMS for HNO_3

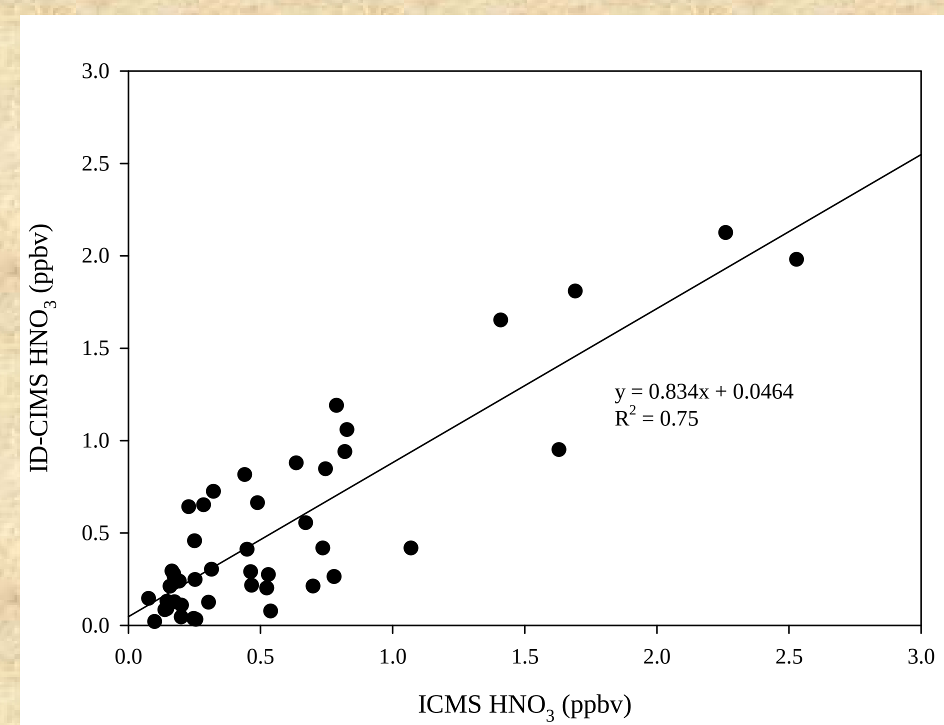
$SF_6 + e^- \rightarrow SF_6^-$

$SF_6^- + SiF_4 \rightarrow SiF_5^- + SF_5$

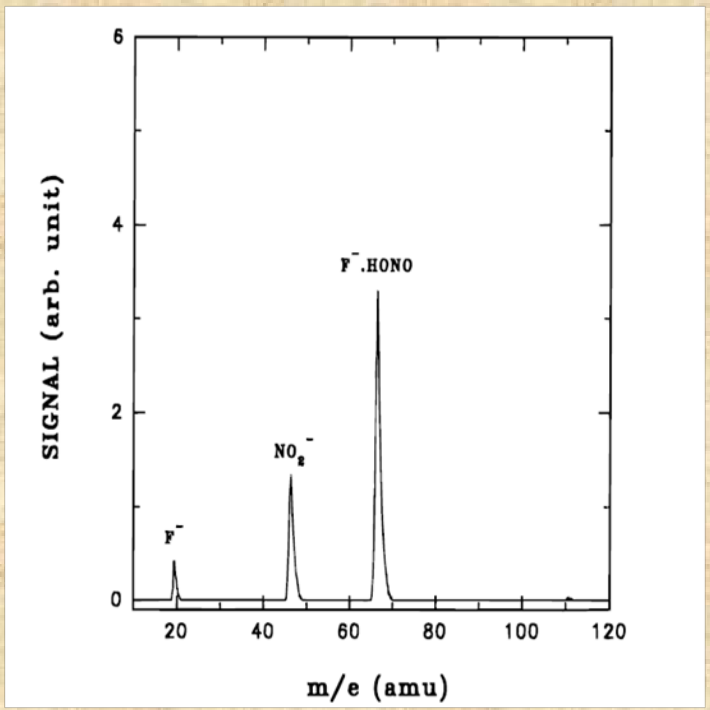
$SiF_5^- + HNO_3 \rightarrow SiF_5^-HNO_3$ adduct, k_1

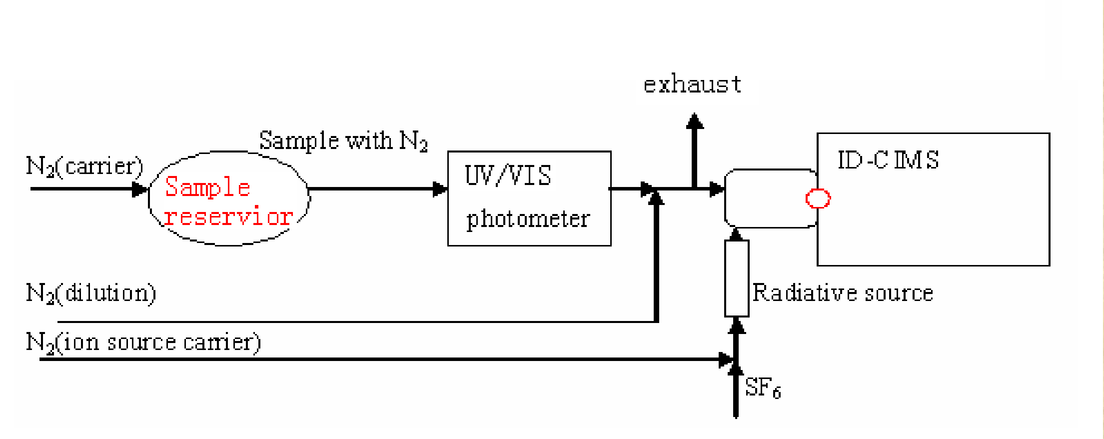
$[SiF_5^- \cdot HNO_3] = k_1 [SiF_5^-] \Delta t [HNO_3]$

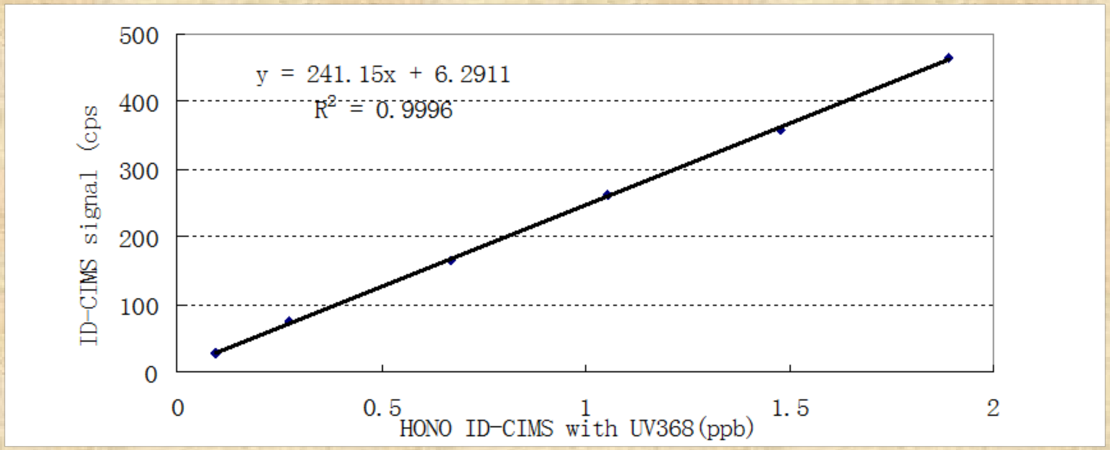




Measurements of HONO by ID-CIMS



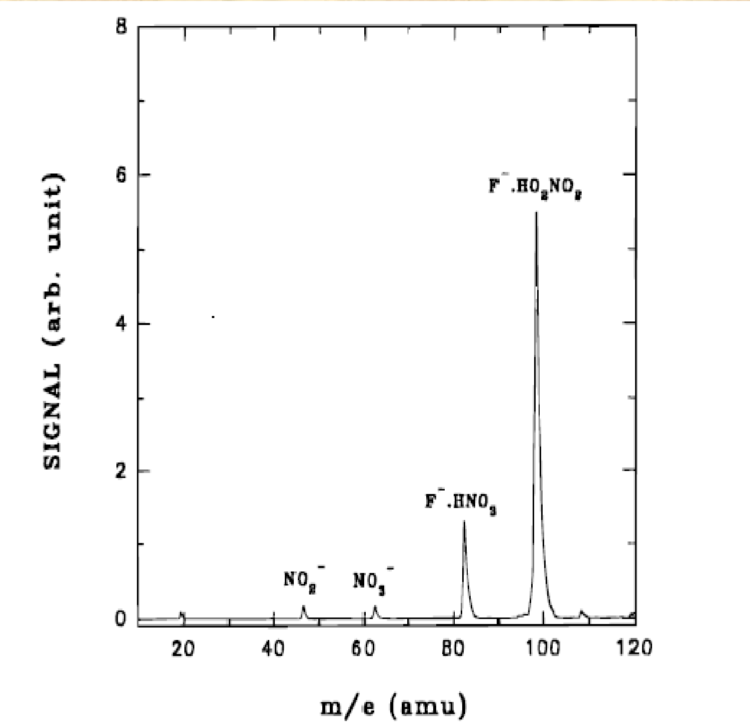


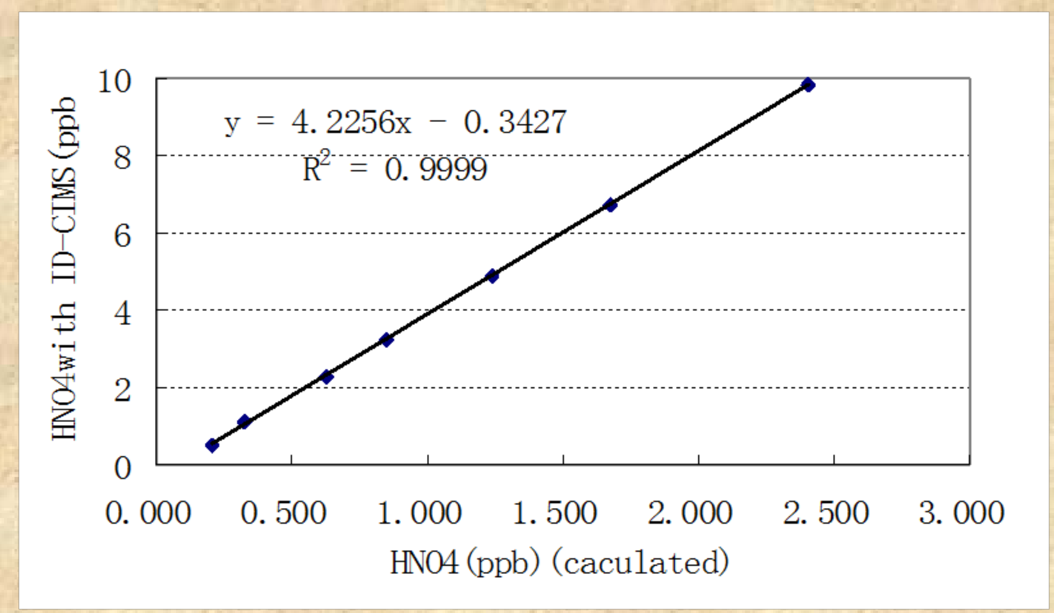


$HONO + SF_6^- \rightarrow HONO{\cdot}F^- + SF_5$

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





$HNO_4 + SF_6^- \rightarrow HNO_4 \cdot F^- + SF_5$

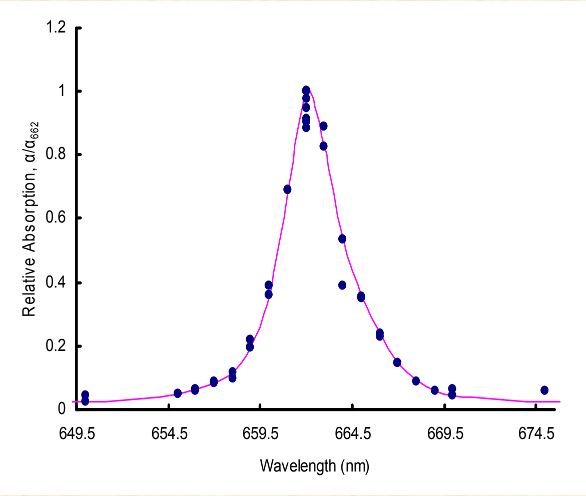
Sensitivity of 150-200 cps/ppb and a detection limit of 10-20ppt for a 1 s integration time

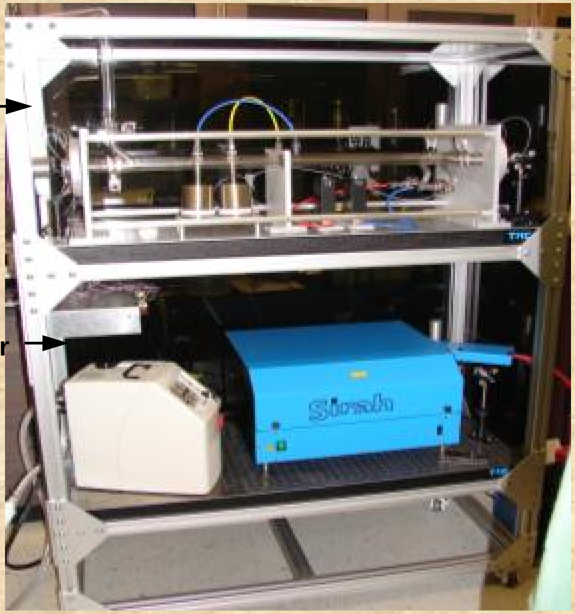
NO_3/N_2O_5 by Cavity Ring-Down Spectrometer (CRDS)

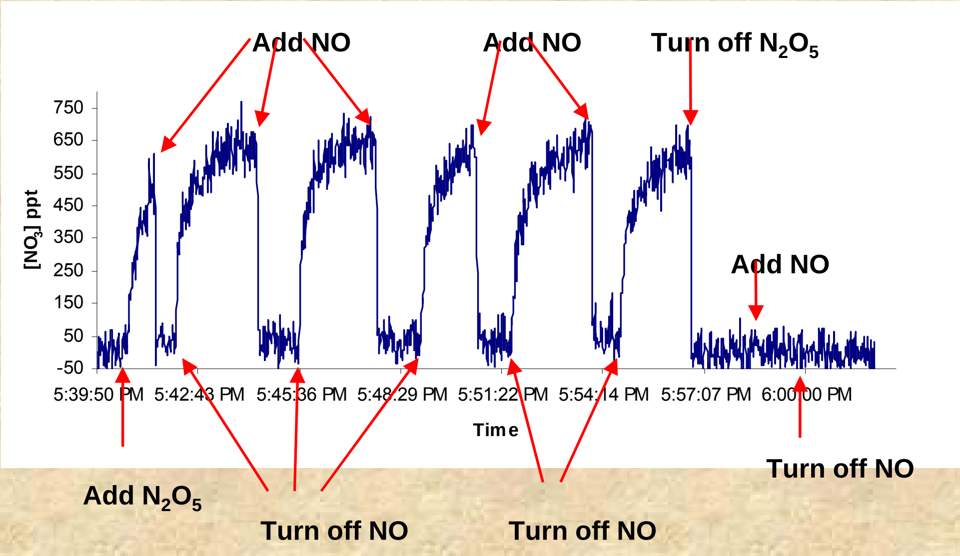
Simultaneous measurements of NO_3 and N_2O_5

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

Sensitivity on the order of 1 ppt for short integration times



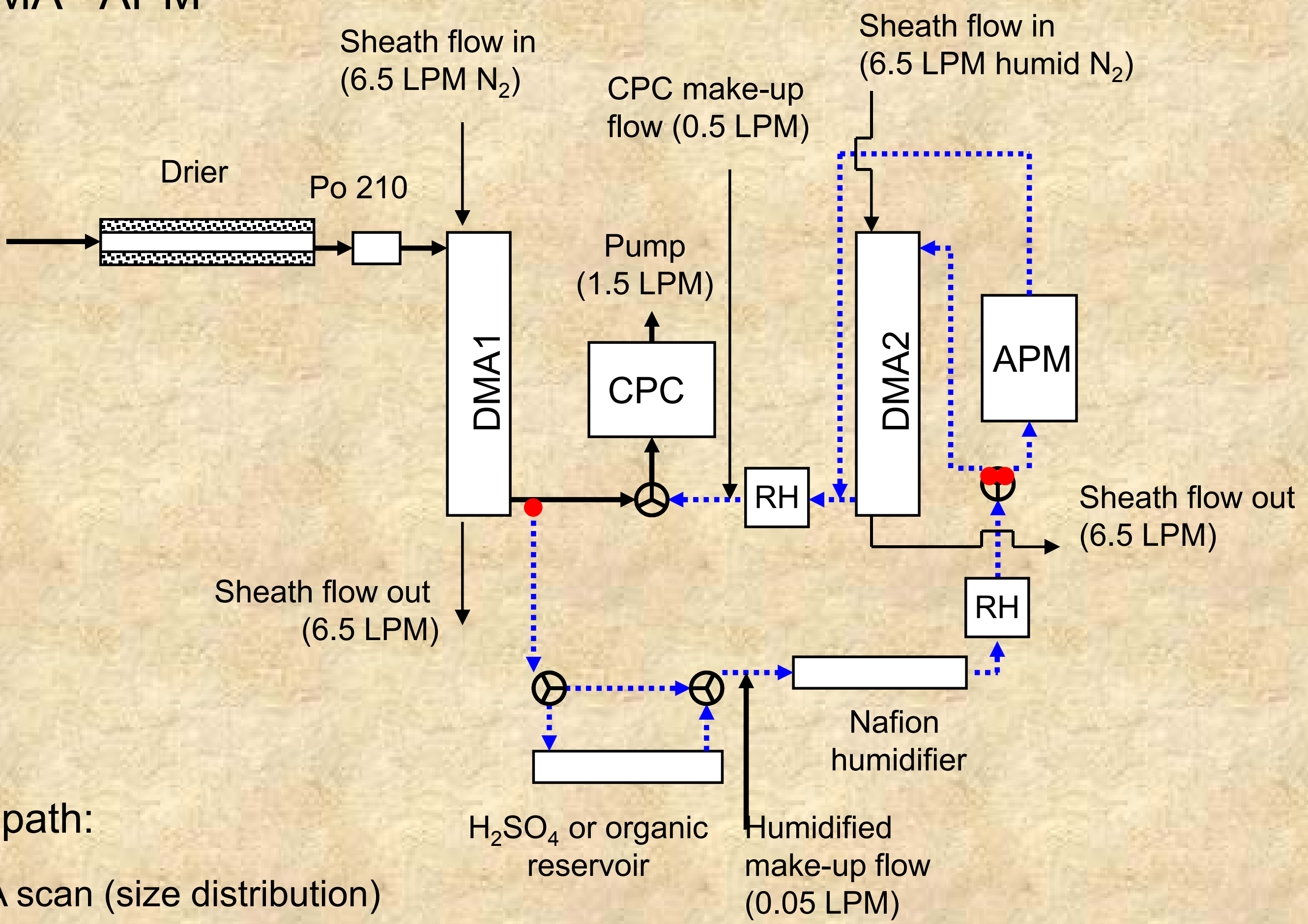




TDMA/DMA-APM system

Operation modes:

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

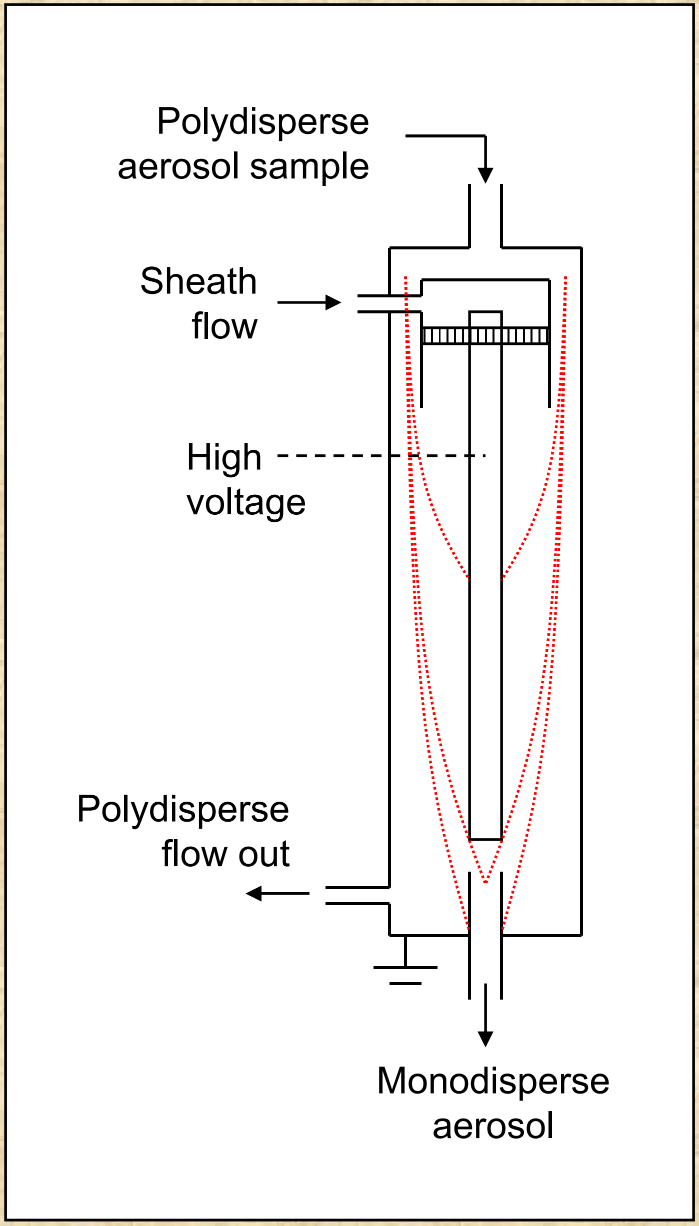


Aerosol path:

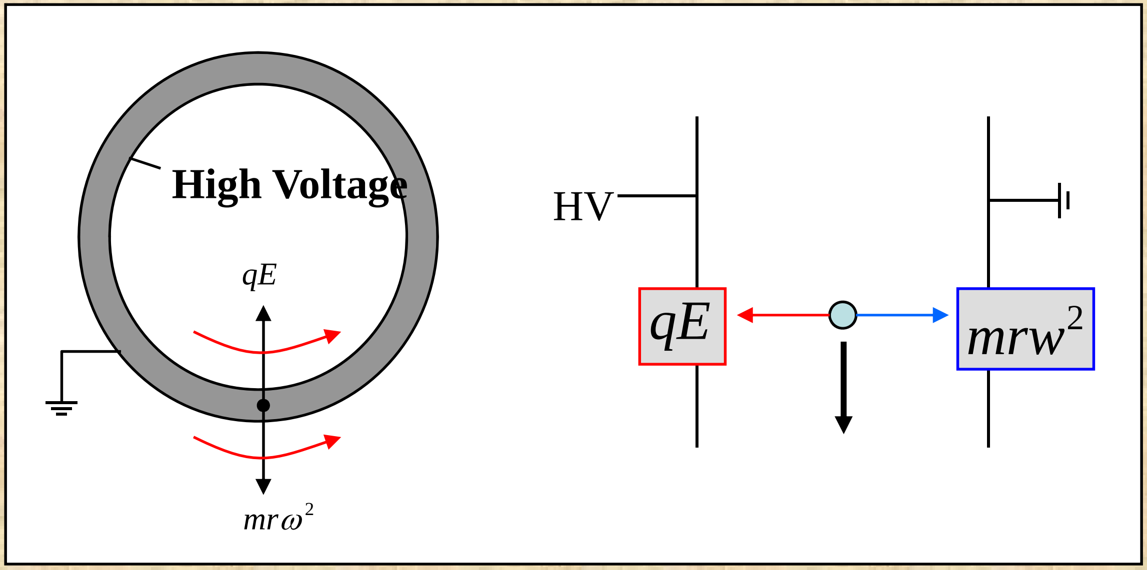
— DMA scan (size distribution)

•••• TDMA or DMA-APM scan

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**

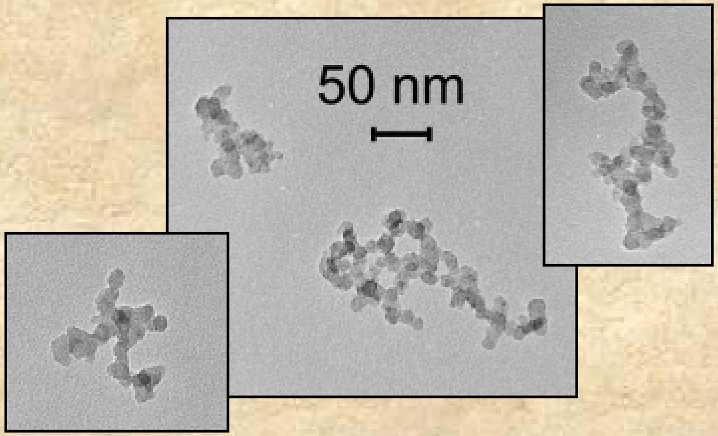
$$m \propto d_B^{Df}$$

(d_B is mobility diameter)

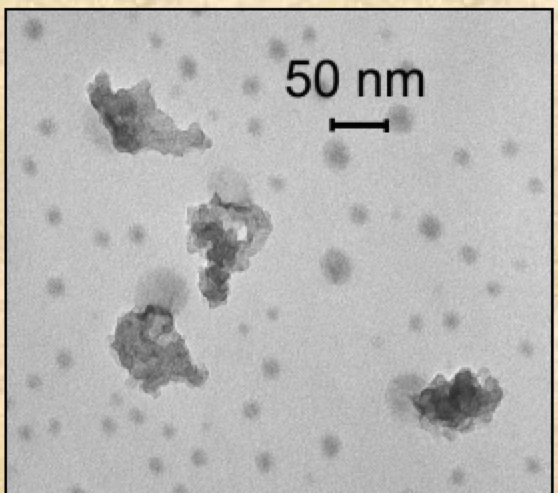
$$\rho_{eff} \propto d_B^{Df-3}$$

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

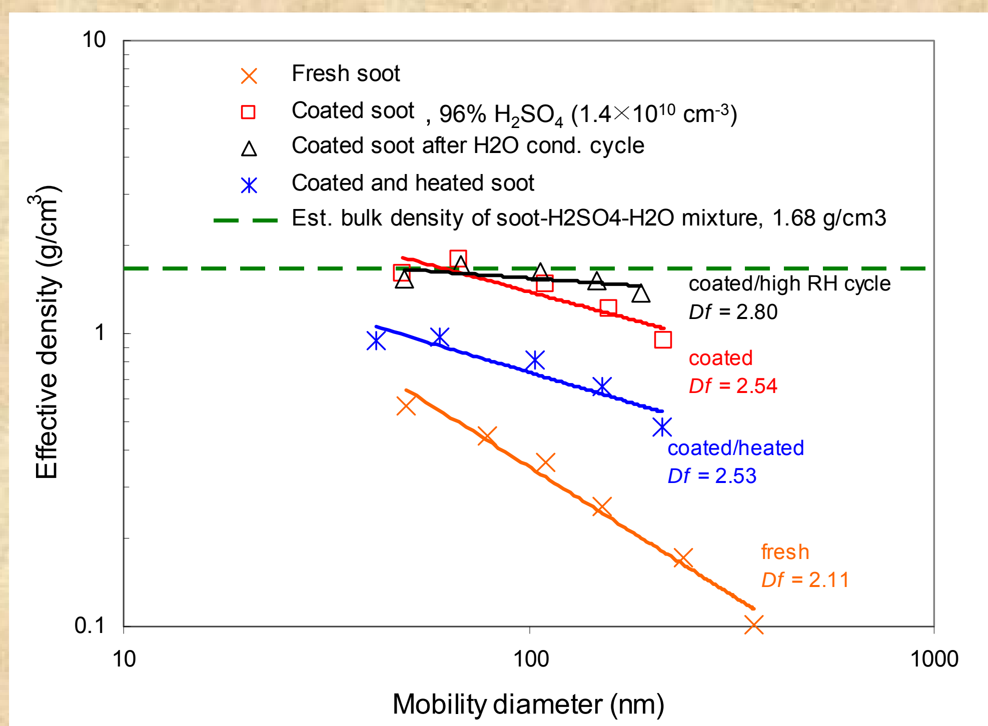
Soot Aging by Absorption of H_2SO_4 and H_2O



Fresh soot agglomerates

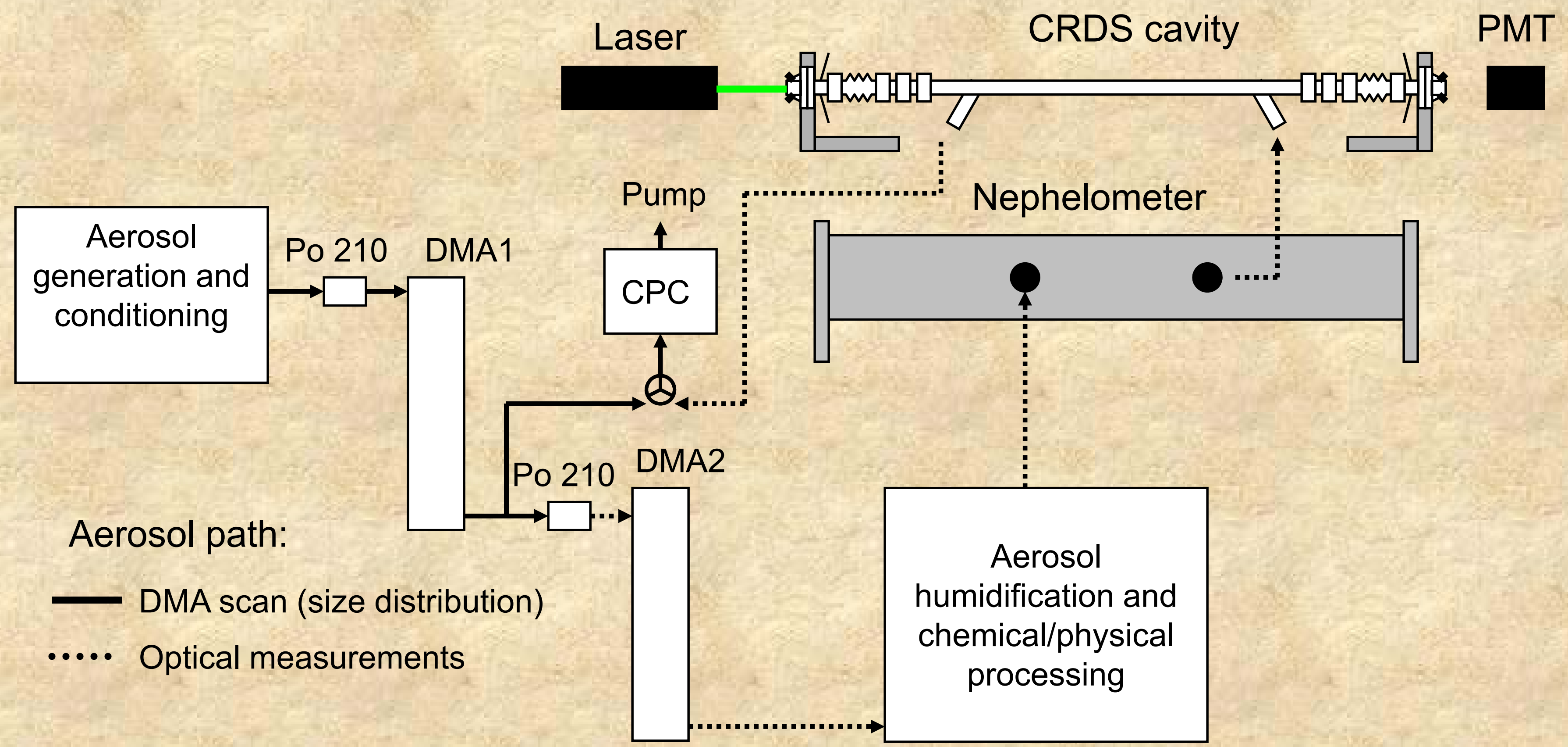


Soot exposed to 1.5×10^{10} cm^{-3} H_2SO_4 vapor for ~12 s



Optical Properties by DMA-DMA/Nephelometer/CRDS

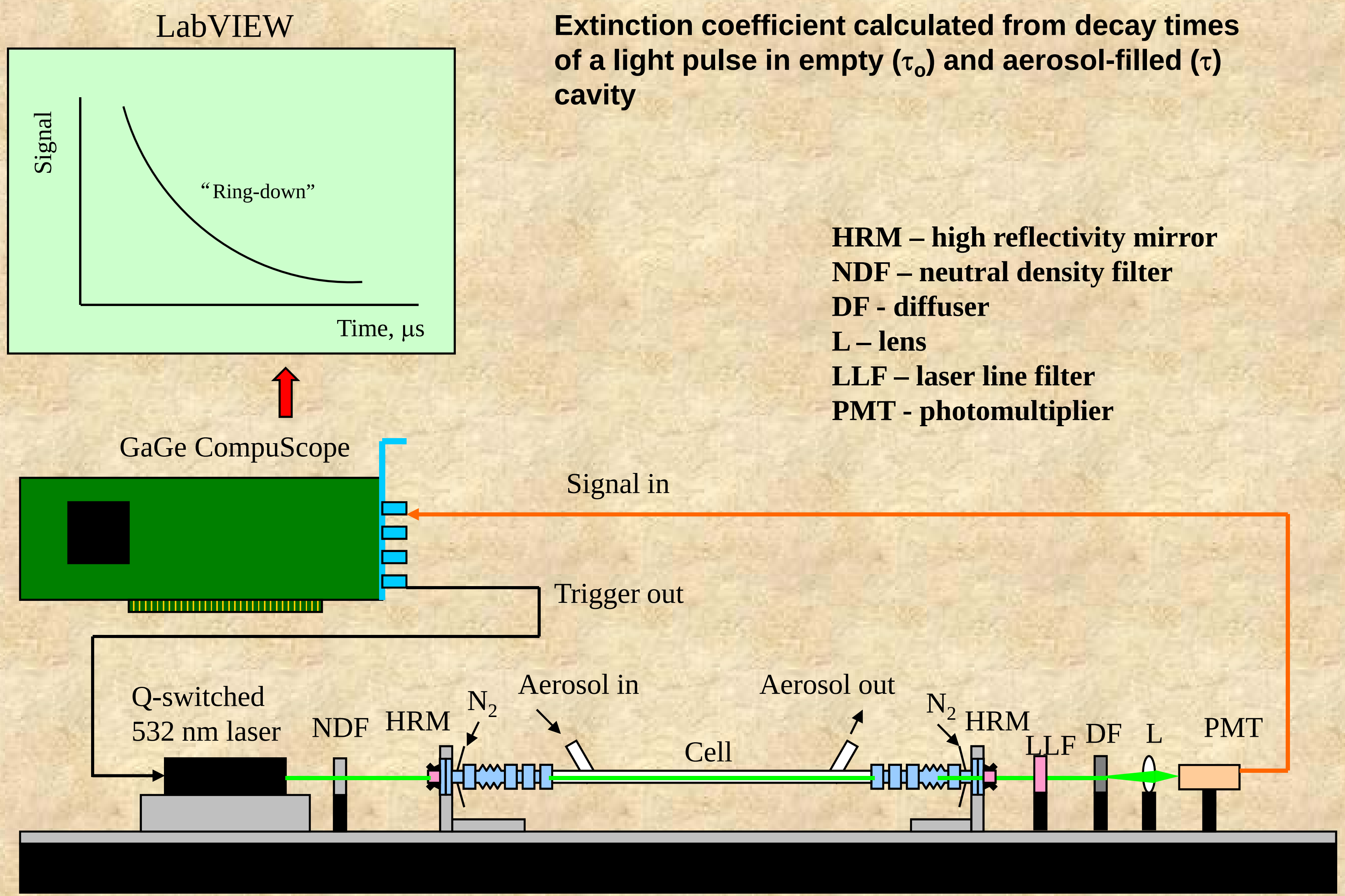
- **DMA-DMA system, CRDS, nephelometer, and connecting tubing kept at a constant temperature**
- **Relative humidities in the CRDS and nephelometer within 1%**



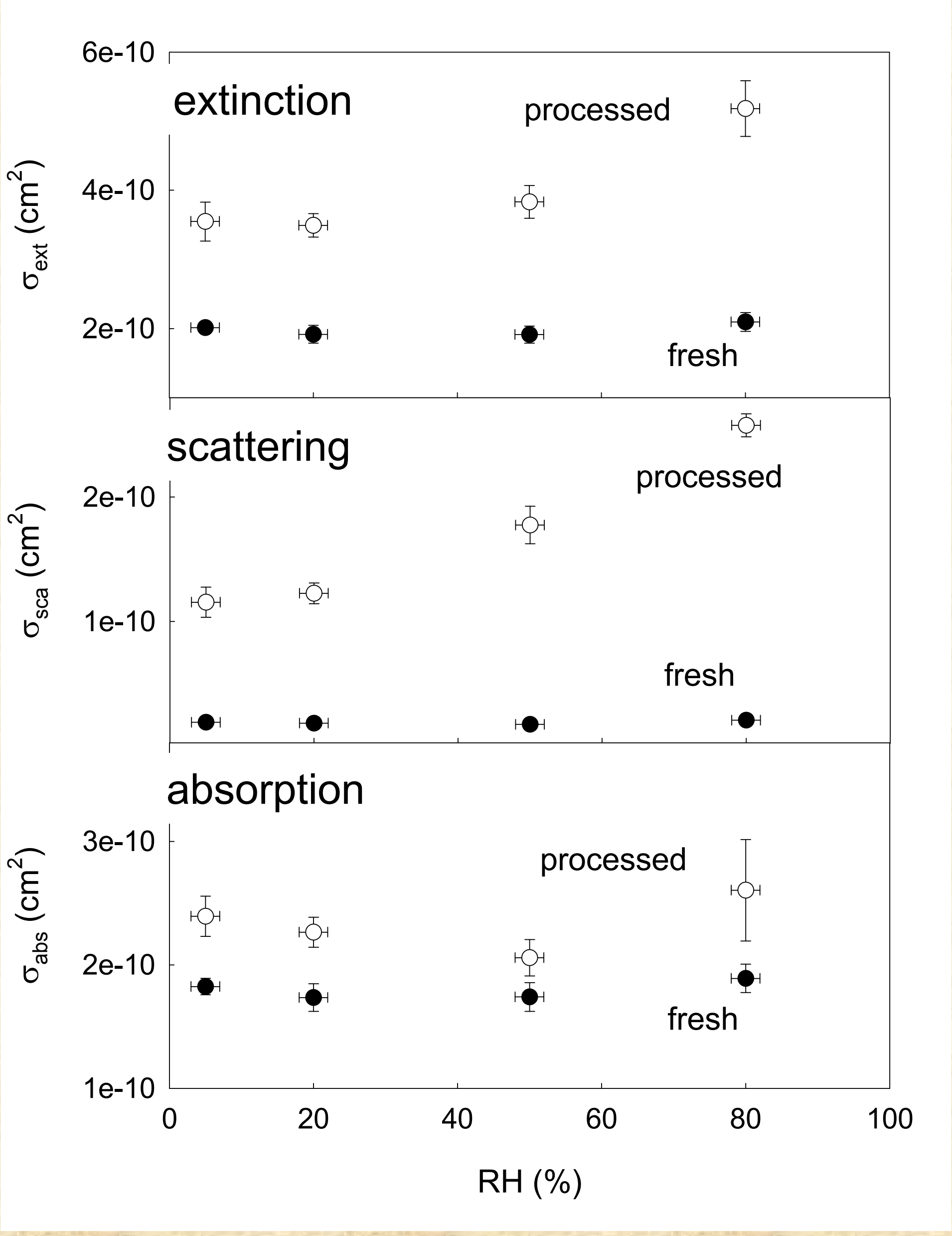
Cavity Ring-Down Spectrometer

Extinction coefficient calculated from decay times of a light pulse in empty (τ_o) and aerosol-filled (τ) cavity

HRM – high reflectivity mirror
NDF – neutral density filter
DF - diffuser
L – lens
LLF – laser line filter
PMT - photomultiplier



Optical Properties of Soot



- **Amplification of extinction, scattering and absorption**
  (D_o = 320 nm, RH 80%)

  Extinction: 2.6
  Scattering: 13.8
  Absorption: 1.5

- **Using absolute mass of coated particles calculated mass specific absorption (m^2 g^{-1})**

  fresh (155/245/320 nm): 6.5, 8.2, 8.6

  coated (320 nm): 11.6 (5% RH)
  10.0 (50% RH)
  12.6 (80% RH)

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

Issues Relevant to *the TERC Strategic Research Plan 2007-2009*:

Section 3: CHEMISTRY AND PHYSICS OF ATMOSPHERIC CONSTITUENTS

"Examine heterogeneous processes involving HONO formation and NO_x sinks (e.g., N_2O_5 hydrolysis) as part of the ambient and model sensitivity studies discussed above, and also in appropriate laboratory and chamber studies." (p. 12)

"It also requires appropriately characterizing the heterogeneous processes that may affect the gas-phase reactions, such as HONO formation and NO_x sinks on various types of surfaces (e.g., sticking coefficients, particulate morphology, radiative properties)." (p. 12)

Section 4: AMBIENT MEASUREMENT/MONITORING

"Continued research into the mechanism and extent of production of HONO is called for, supported by special ambient measurements of HONO, other relevant gas-phase species such as HNO_3, and potential substrates for heterogeneous reactions, such as aerosol and soot particles." (p. 16)

"In summary, it is time for definitive work to determine the relative importance of primary versus secondary formaldehyde and other radical sources such as HONO in determining ozone productivity in Houston. Recent research on multiphase reactions has been fruitful and puts TERC on the cutting edge of air pollution science. Such research should be continued, especially in the light of measurements that indicate levels of HONO that cannot be explained by gas-phase chemistry alone." (p. 17)