Laboratory evaluation of the effect of nitric acid on chilled mirror hygrometer measurements in the UT/LS

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Motivation

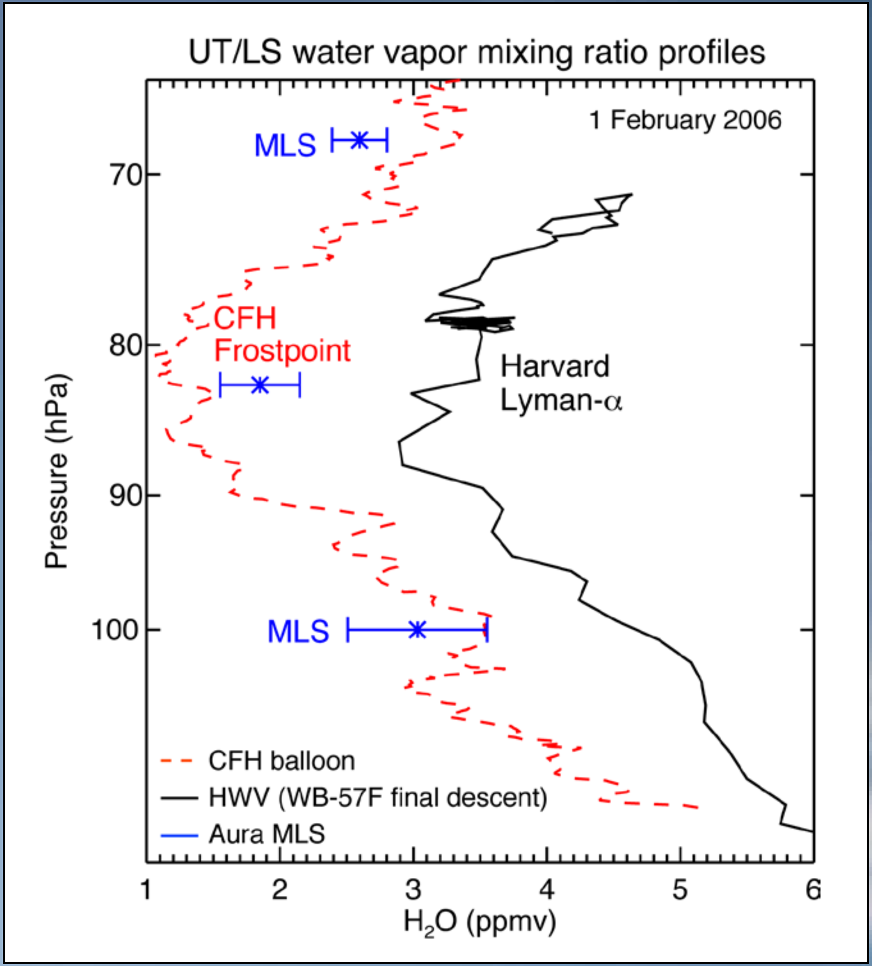


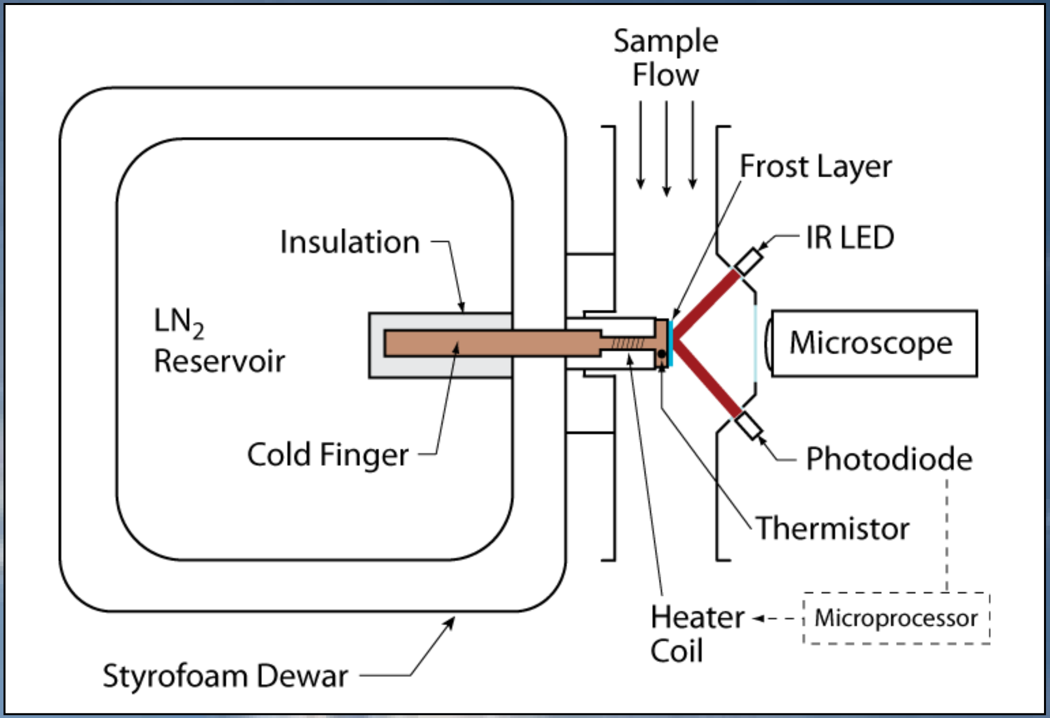
Figure courtesy of E. Jensen, NASA

- Disagreement among UT/LS water vapor measurements at mixing ratios < 5 ppm
- Laboratory and field measurements have shown HNO_3 is readily taken up by ice surfaces
- Evidence that high HNO_3 levels can interfere with frost point measurement (Szakall et al., ES&T, 2001)

CSD Water Vapor Efforts

- Funding in FY2010 for additional water vapor research efforts
- Development of CIMS instrument for UT/LS water vapor measurements from aircraft
  - In flight zero and multi-point calibration
- Coordinate development of national water vapor standard for establishing common basis for in situ water vapor measurements
  - Acquisition of reference commercial frost point instrument (MBW)
- Analysis of satellite data (HALOE, AIRS, MLS) to study long term trends and oscillations in UT/LS water vapor [Rosenlof, Davis]
- Investigation of potential interferences in water vapor measurement by chilled mirror hygrometers

Laboratory Frost Point Instrument

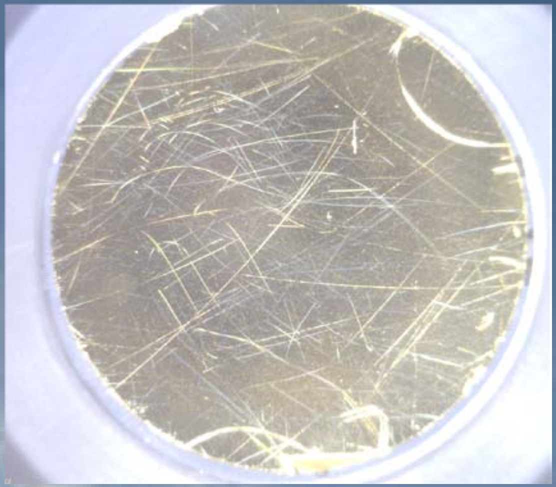


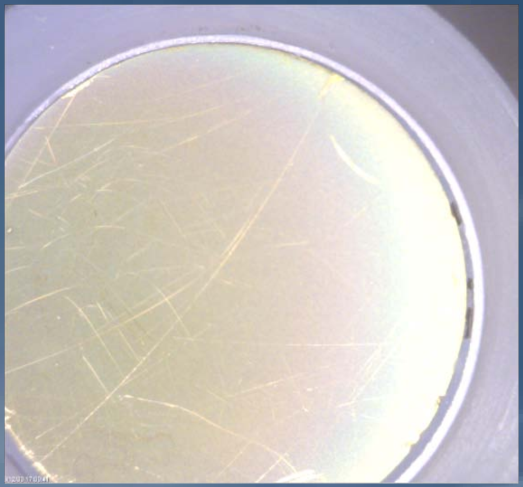
Stable frost point temperature is converted to water vapor partial pressure using an approximation to the saturation vapor pressure over ice

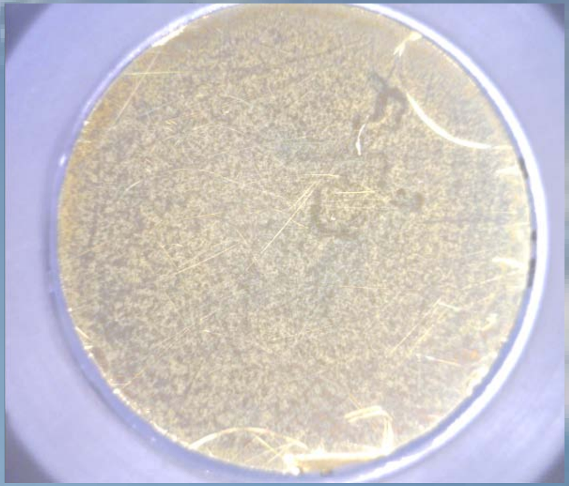
$$p_{ice} = \exp(9.550426 - 5723.265/T + 3.53068 \ln(T) - 0.00728332T)$$

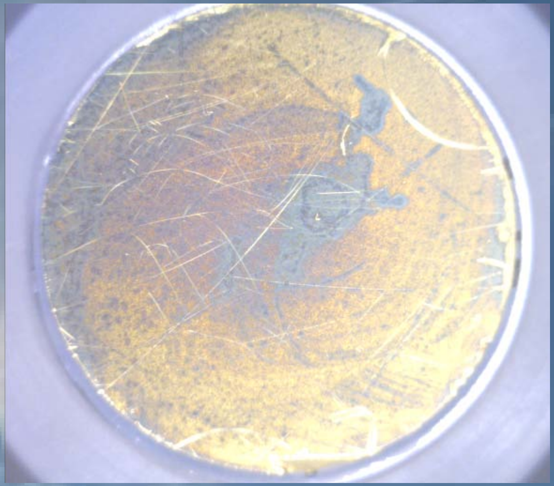
Murphy and Koop, QJRMS, 2005

CFH Frost Images

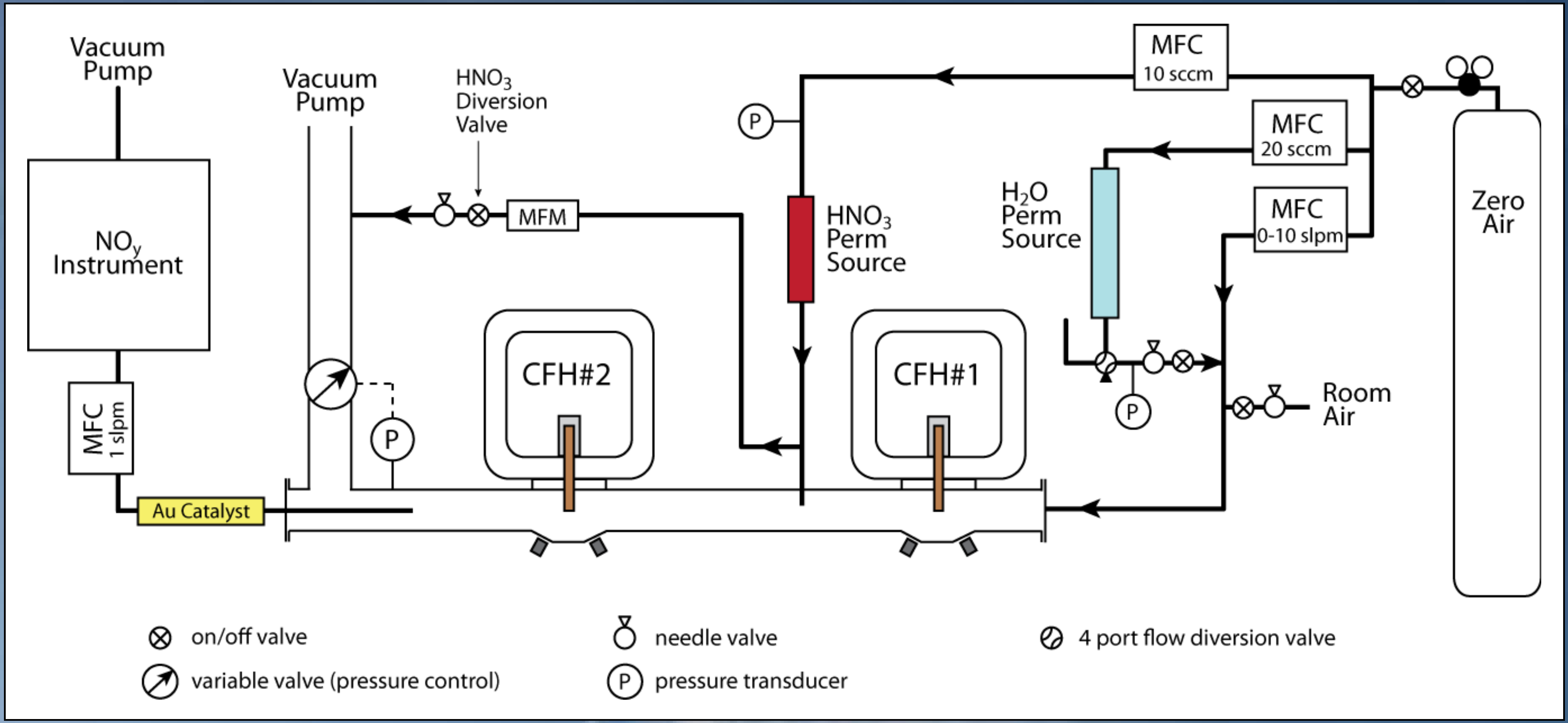






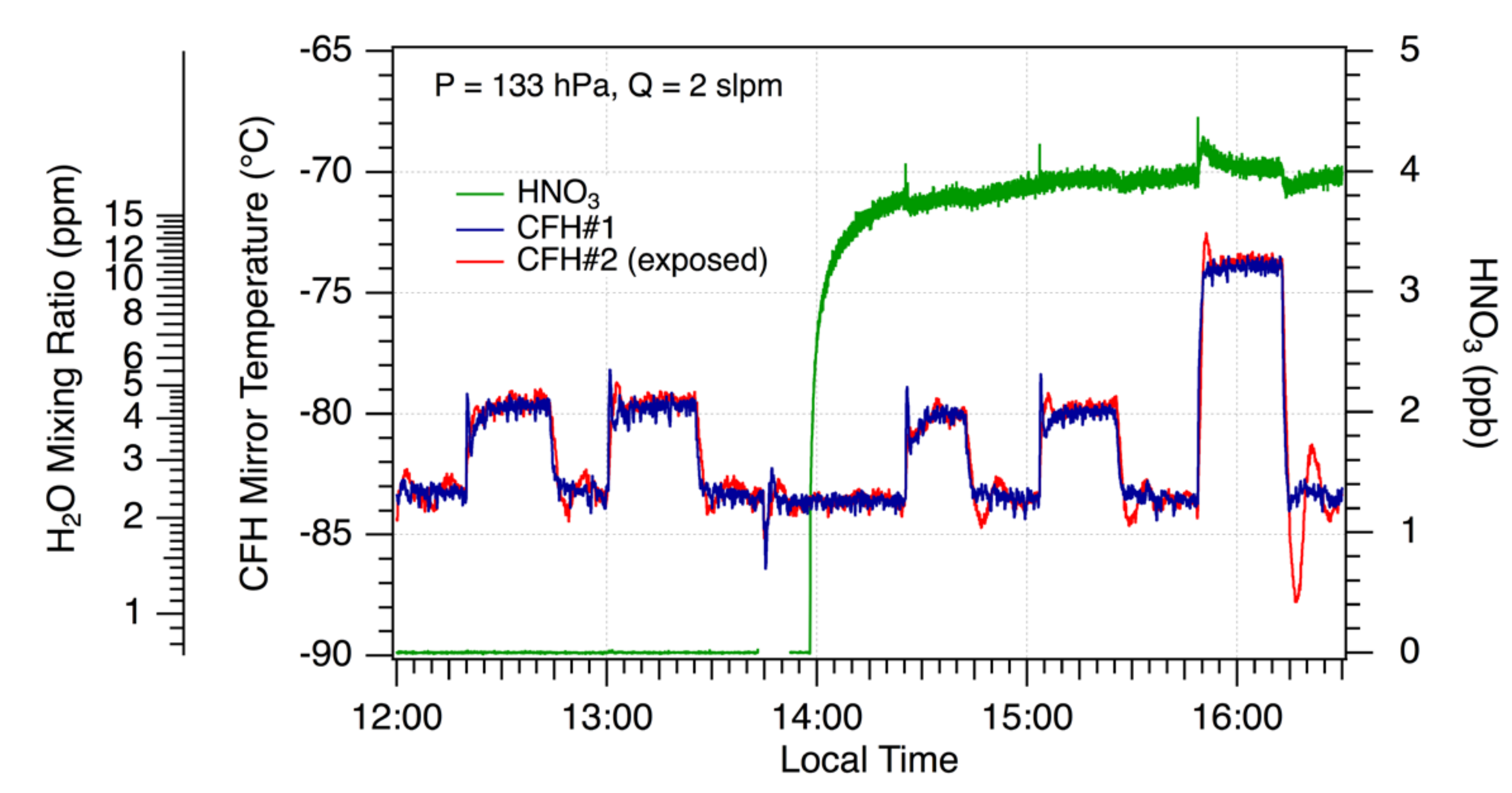


Experimental Configuration



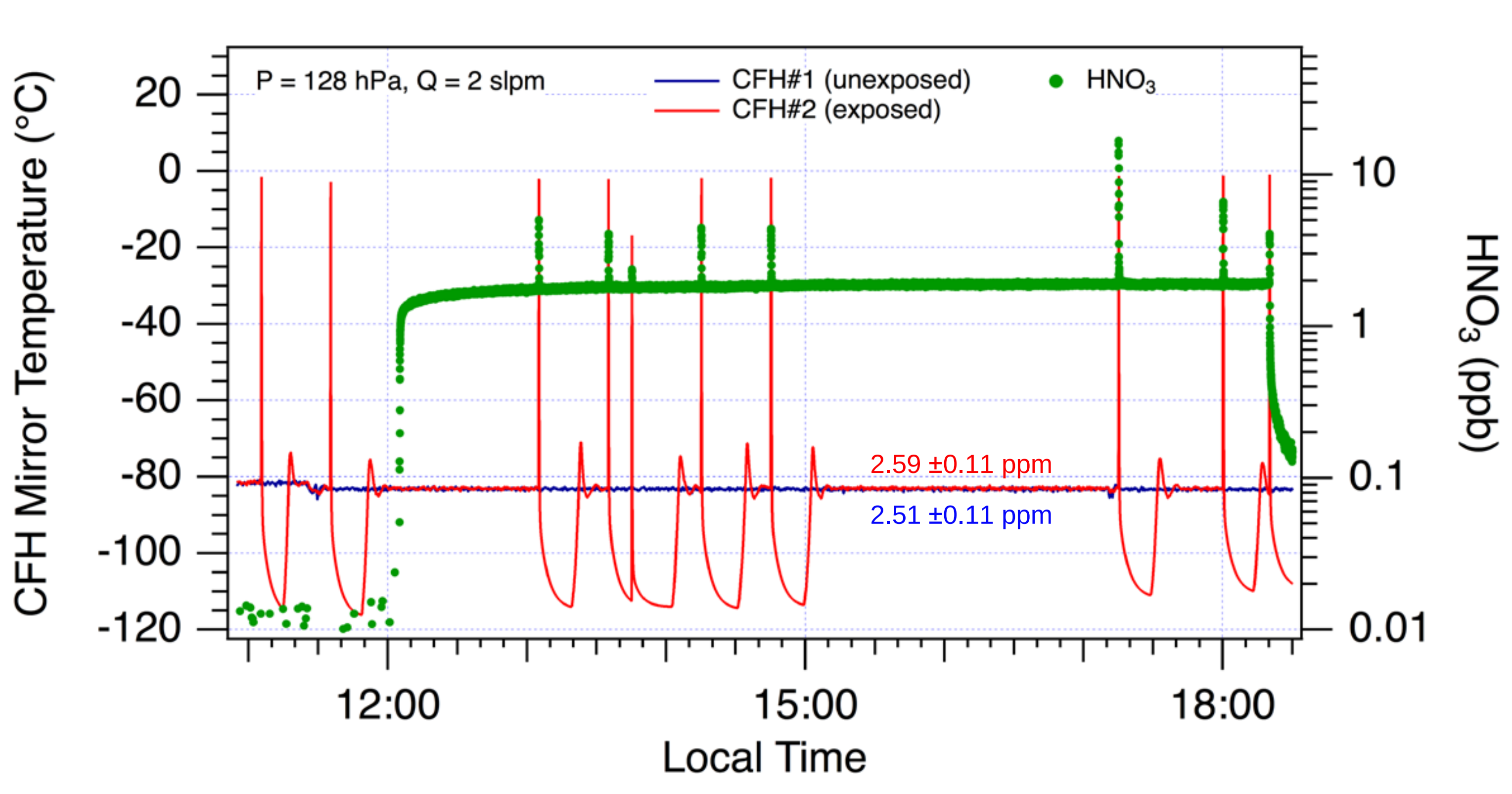
- Vacuum system allows operation of CFH units at UT/LS pressures and H_2O mixing ratios with flow rates similar to balloon instruments
- HNO_3 added between the two CFH units

Frost point with ppb levels of HNO_3



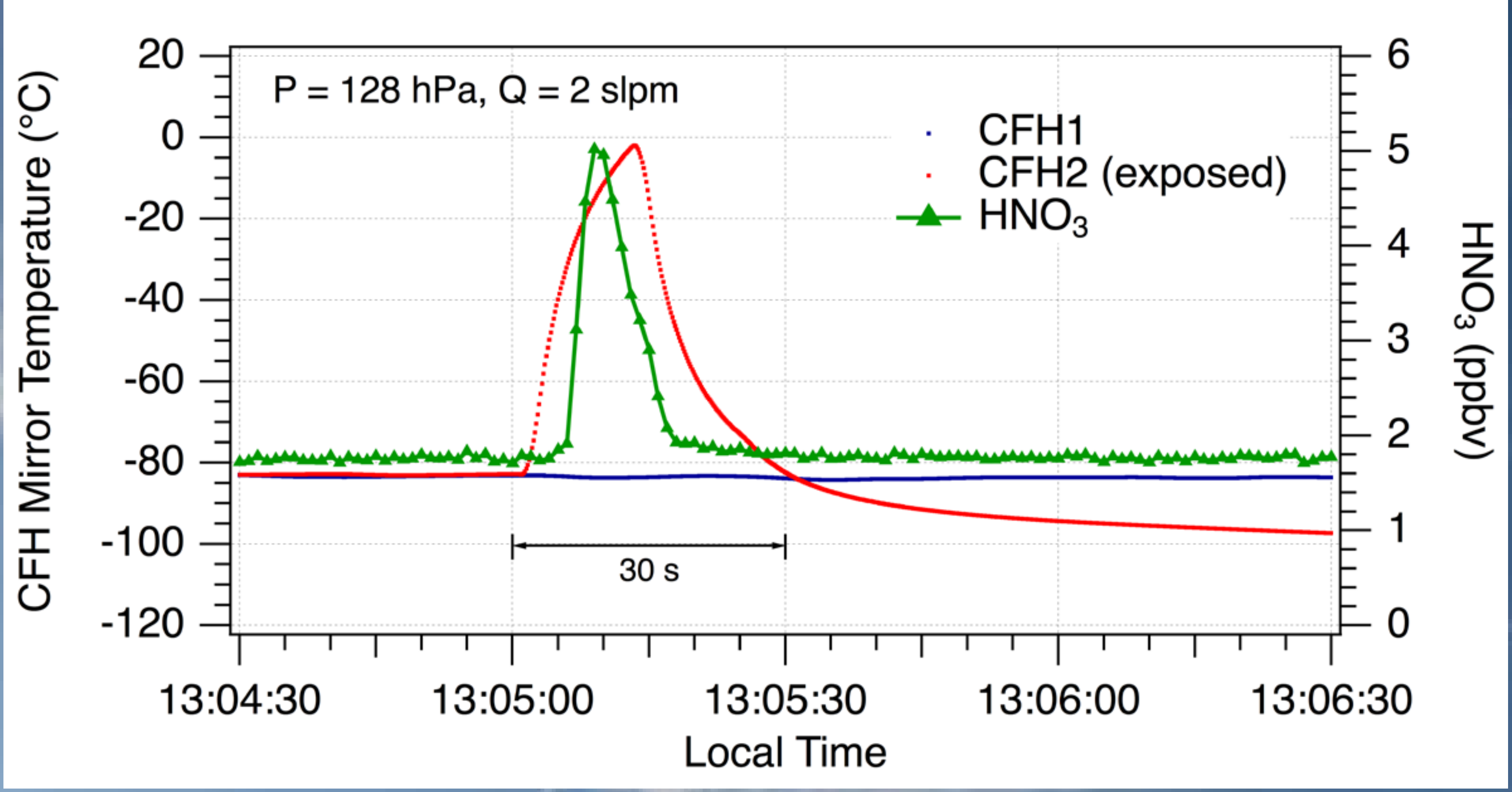
- The CFH units have slightly different transient responses to rapid changes in water vapor
- No observed effect from exposure to 4 ppb HNO_3 for > 2 hours

Detecting the Presence of HNO_3



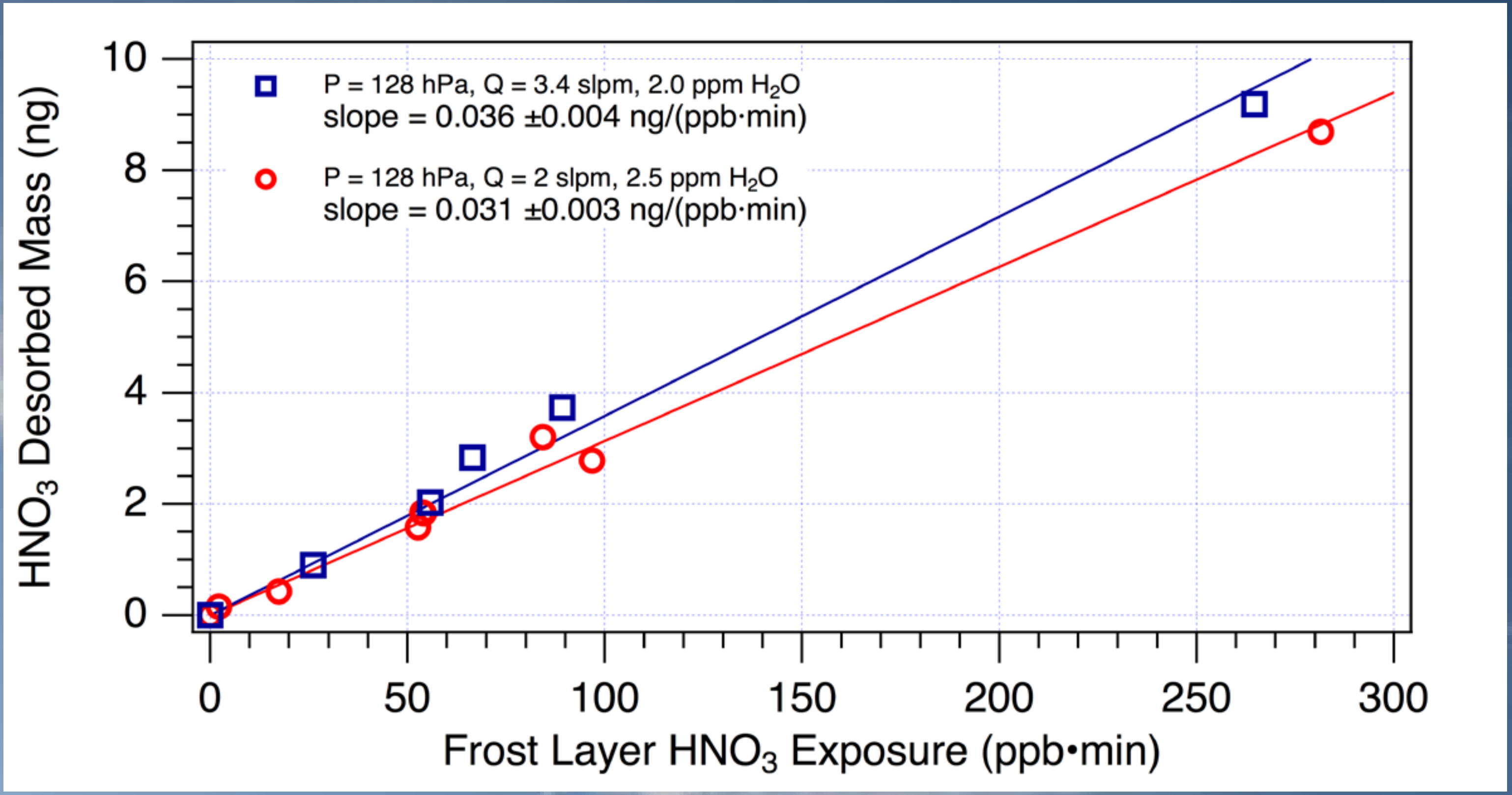
- Stable measurement agreement between the two CFH units ~3%
- Frost layer removal by mirror heating allows direct measurement of the HNO_3 in the frost layer

HNO_3 Desorption Peak



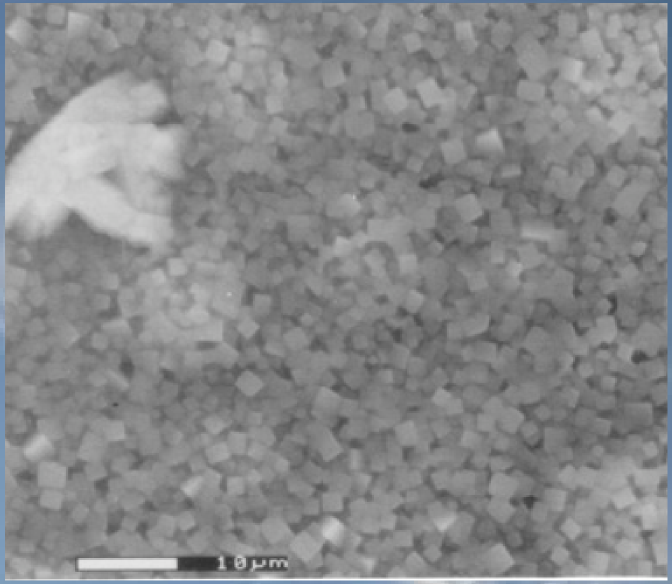
- NO_y instrument sees a ~15 second wide peak in signal
- Can integrate the NO_y signal to determine the mass of HNO_3 in the frost layer

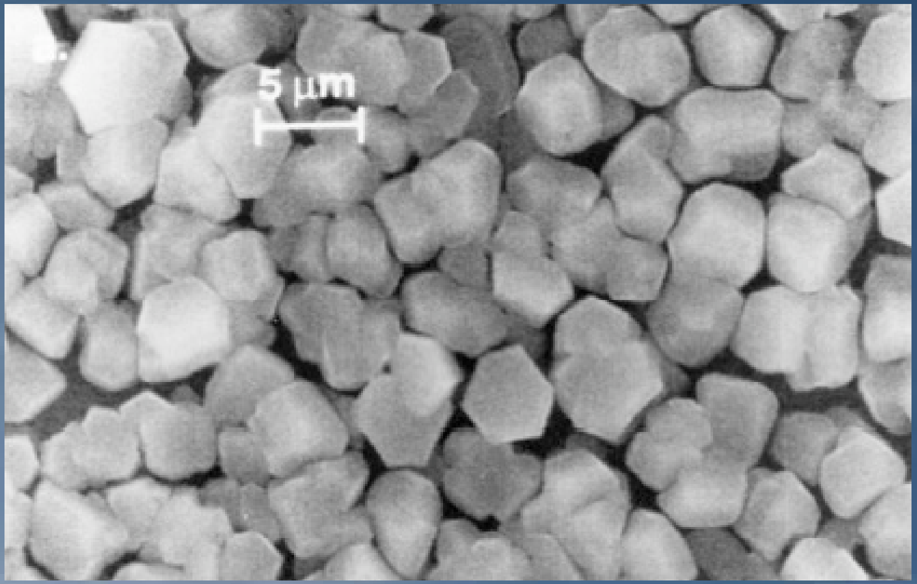
HNO_3 Accumulation on Frost



- HNO_3 uptake to frost layer linear over 3 hour timescale
- 8 ng HNO_3 corresponds to approximate monolayer coverage of mirror geometric surface area, but…

Frost Structure





Electron micrographs of a H_2O ice film formed by vapor deposition at 200–202 K (left) and 180 K warmed to 200K (right).

Leu and Keyser, Int. Rev. Phys. Chem., 2009

Conclusions

- No detectable interference on CFH water vapor measurement from atmospherically relevant gas-phase HNO_3 exposures
- HNO_3 co-condenses/adsorbs on the frost layer, as expected from previous laboratory studies of HNO_3 uptake onto ice and observations of HNO_3 in cirrus cloud particles
- HNO_3 fractional surface coverage from gas-phase uptake is likely small for the exposures in our experiments and thus also for balloon sonde measurements

Summer 2010

- Further experiments of frost point performance including additional interference tests (sulfuric acid aerosols and ternary solution aerosols)
- Characterization of frost point time response
- Inclusion of laboratory version of GMD FPH into experiments
  - Optimize PID tuning for UT/LS operation