

## Measurements of NO<sub>2</sub>, ΣPNs, ΣANs, and HNO<sub>3</sub> by Thermal Dissociation and Laser Induced Fluorescence during INTEX-B

Ronald C. Cohen  
University of California, Berkeley

During INTEX-B, we will use thermal-dissociation coupled to laser-induced fluorescence (TD-LIF) detection of NO<sub>2</sub> for observations of NO<sub>2</sub>, total peroxy nitrates (ΣPNs ≡ PAN + PPN + N<sub>2</sub>O<sub>5</sub> + HNO<sub>4</sub> . . .), total alkyl- and hydroxyalkyl nitrates (ΣANs), HNO<sub>3</sub> and the sum of these four classes of NO<sub>y</sub> species. Observations obtained via TD-LIF will be used to address questions pertaining to the source distribution and chemical speciation of NO<sub>y</sub> in the Continental Boundary Layer (CBL), their export from the CBL to the free troposphere and their subsequent transport. Integrated column measurements of NO<sub>2</sub>, taken during orbit descents and ascents, will be used for direct validation of NO<sub>2</sub> columns retrieved from both the OMI and SCIAMACHY instruments aboard the AURA and ENVISAT satellites.

### Instrumentation

#### *NO<sub>2</sub> Detection*

Briefly, the TD-LIF instrument we will fly aboard the DC-8 during INTEX-B uses a compact, diode pumped, Q-switched (10 kHz, 30nsec pulse length), frequency doubled (532nm), Nd<sup>3+</sup>: YAG laser to pump a tunable dye laser (500mW @ 585nm with a linewidth of 0.06 cm<sup>-1</sup>) [Thornton et al., 2000]. The home-built, etalon tuned dye laser is used to tune the laser to excite a narrow rovibronic feature unique to NO<sub>2</sub>. The light from the dye laser is focused sequentially into two 40 pass White cells. Red-shifted fluorescent photons at wavelengths longer than 700 nm are collected and imaged onto the photocathode of a cooled GaAs photomultiplier tube. Dichroic filters manufactured using fused silica substrates and without any absorbing components are used to reject Rayleigh, Raman and chamber scatter. Single photons are counted using time-gated photon counting techniques. The laser is alternately tuned between a strong NO<sub>2</sub> resonance and the weaker continuum absorption to test for interferences, assess the background scattering, and for use in an algorithm that holds the laser frequency locked on a single spectral feature.

We incorporate a supersonic expansion in the detection region, increasing the population of NO<sub>2</sub> in the rotational state we excite [Cleary et al., 2002]. The gas sample flowing at 1SLM is expanded through a 0.3 μm pinhole into a chamber held at 250mtorr. The resulting rotational

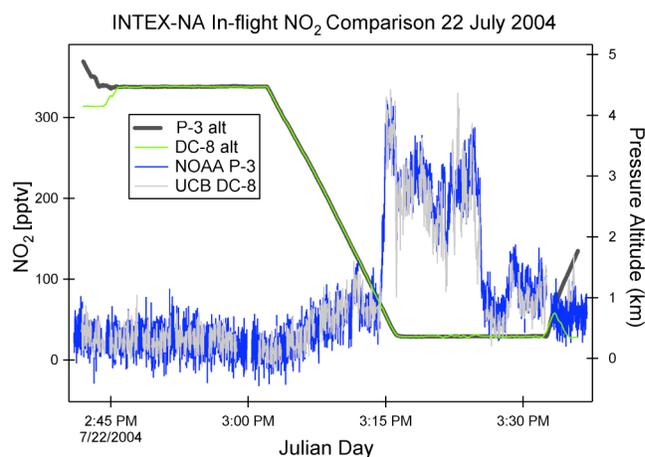


Figure 1. In flight comparison of NO<sub>2</sub> as measured from the NASA DC-8 (UCB LIF) and from the NOAA P-3 (NOAA CL) during INTEX-NA.

temperature in the jet is  $\sim 25\text{K}$  which enhances the signal by a factor of 30. The primary instrument calibration is the response to additions of NIST traceable  $\text{NO}_2$  standards of 5 ppmv diluted with zero air. The calibration is repeated as often as necessary to capture alignment changes or potential interferences from the atmosphere. We also frequently measure the instrument zero by over-pressuring the inlet with zero air. The detection sensitivity of this instrument is 0.8ppt/min at  $S/N=2$ . The uncertainty in the instrument zero is less than 1ppt.

#### $\Sigma\text{PN}$ , $\Sigma\text{AN}$ and $\text{HNO}_3$ detection

We couple a thermal dissociation pre-reactor to the LIF detector to observe  $\Sigma\text{PNs}$ ,  $\Sigma\text{ANs}$  and  $\text{HNO}_3$  [Day et al., 2002]. These species thermally dissociate to yield  $\text{NO}_2$  and a companion radical:



The sample is rapidly heated in a quartz tube, producing an enhancement in  $\text{NO}_2$  over the ambient background. After flowing through a short region that allows the sample to cool to near ambient temperature, the sample is transported in PFA Teflon tubing to the LIF detection system where  $\text{NO}_2$  is observed. At a residence time of 30-90ms and a pressure of 1 atmosphere, approximate temperatures for complete dissociation are:  $200^\circ\text{C}$  for  $\Sigma\text{PNs}$ ;  $400^\circ\text{C}$  for  $\Sigma\text{ANs}$ ; and finally  $650^\circ\text{C}$  for  $\text{HNO}_3$  (Figure 2).

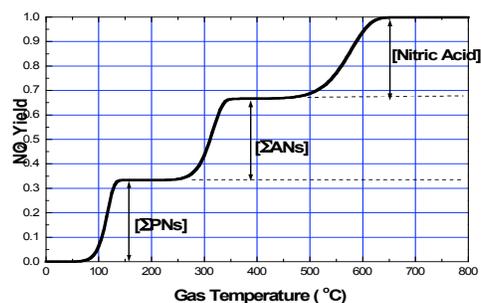


Figure 2. Theoretical yield of  $\text{NO}_2$  from an equal mixture of 3 classes of nitrogen oxides.

#### References:

- Cleary, P.A. et al., (2002) *Applied Optics* 41(33): 6950-6956.
- Day, D.A. et al., (2003) *Journal of Geophysical Research* 108 (D16):10.1029/2003JD003685.
- Day, D.A. et al., (2002) *Journal of Geophysical Research* 107 (D6):10.1029/2001JD000779.
- Murphy, J.G. et al., (2003) *Atmospheric Chemistry and Physics Discussions* November 2003.
- Rosen, R.S. et al., (2004) *Journal of Geophysical Research* 109 D07303.
- Thornton, J.A. et al., (2000) *Analytical Chemistry* 72 (3): 528-539.