

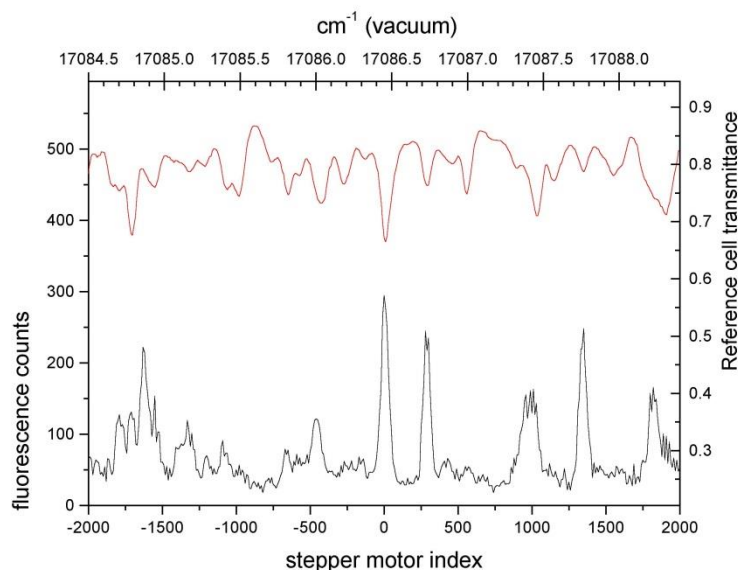
## In-Situ Measurements of NO<sub>2</sub>, ΣPNs, ΣANs, and HNO<sub>3</sub> by Thermal Dissociation – Laser Induced Fluorescence

Ronald C. Cohen, University of California, Berkeley

The UC Berkeley thermal-dissociation laser-induced fluorescence (TD-LIF) instrument detects NO<sub>2</sub> directly and detects total peroxy nitrates (ΣPNs ≡ PAN + PPN + N<sub>2</sub>O<sub>5</sub> + HO<sub>2</sub>NO<sub>2</sub> . . .), total gas- and aerosol phase alkyl- and multifunctional organic nitrates (ΣANs), and the sum of HNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> following thermal dissociation of these NO<sub>y</sub> species to NO<sub>2</sub>.

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

The airborne TD-LIF instrument uses a compact, diode pumped, Q-switched (7 kHz, 20 nsec pulse length), frequency doubled (532 nm), Nd:YAG laser to pump a tunable dye laser (100 mW @ 585 nm with a linewidth of 0.06 cm<sup>-1</sup>) [Thornton et al., 2000]. The custom-built, etalon-tuned dye laser is used 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 red-sensitive photomultiplier tube (PMT). Dichroic filters are used to reject Rayleigh, Raman, and other background scattered light, and single fluorescent photons are counted using time-gated photon counting. 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 the resonance feature. This instrument also incorporates a supersonic expansion in the detection region to increase the population of NO<sub>2</sub> in the resonant rotational state [Cleary et al., 2002]. The figure below illustrates the room temperature NO<sub>2</sub> reference cell absorption (upper trace) features and the jet-expansion fluorescence (lower trace) spectrum from scanning the laser wavelength.



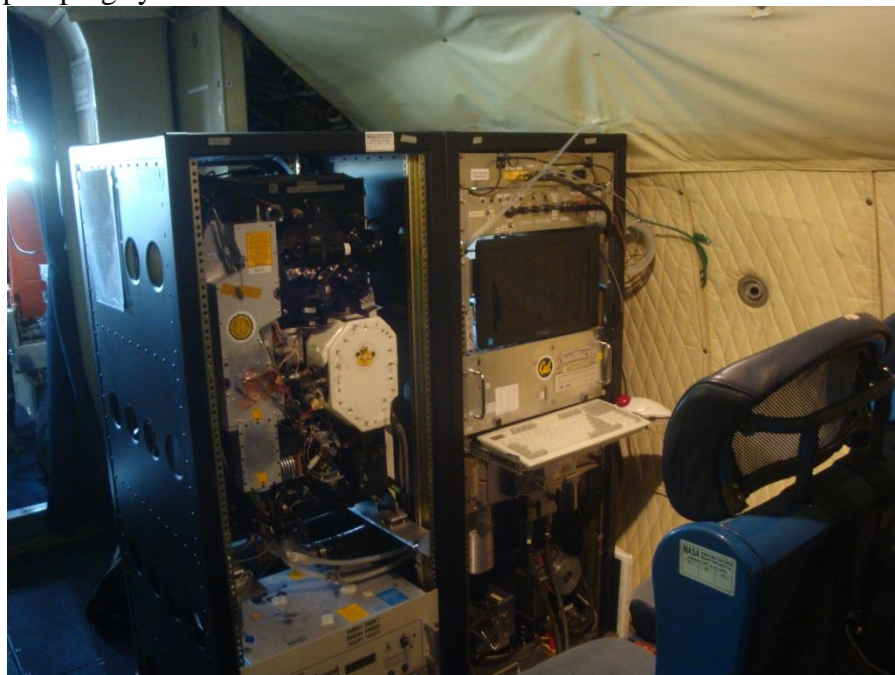
The gas sampled from the external probe is expanded through a 300 μm pinhole into a chamber pumped to ~300 mTorr (at sea level). The rotational temperature in the expansion is estimated to be approximately 25 K and results in a 20-fold signal enhancement. The signal is calibrated to

the response from known NO<sub>2</sub> standards diluted with zero air. The calibration is generally repeated at least once per hour or as often as necessary to capture alignment changes or potential interferences from the atmosphere. During calibration, the instrument background signal is measured by over-pressuring the inlet with zero air. The detection sensitivity of this instrument is 0.8 ppt/min at S/N=2. The uncertainty in the instrument zero is less than 1 ppt.

#### *ΣPN, ΣAN, and HNO<sub>3</sub> detection*

Adding a thermal dissociation pre-reactor to the LIF instrument enables the detection of ΣPNs, ΣANs and HNO<sub>3</sub> [Day et al., 2002; Wooldridge et al., 2010]. These species thermally dissociate to yield NO<sub>2</sub> and a companion radical: XNO<sub>2</sub> + heat → X + NO<sub>2</sub>. The sample is rapidly heated in a quartz tube near the sampling inlet, leading to an enhancement in NO<sub>2</sub> over the ambient background. After flowing through a short region of the tube that allows the sample to cool to near ambient temperature, the sample is transported via PFA Teflon tubing to the LIF detection system where photons from NO<sub>2</sub> fluorescence are detected. At a residence time of 30-90 ms and a pressure of 1 atmosphere, approximate temperatures for complete dissociation of the relevant classes of species are: ~200°C for ΣPNs; ~400°C for ΣANs; and finally ~650°C for HNO<sub>3</sub>.

Physically, the instrument occupies 2 bays of an aircraft high rack (approx. 115 x 65 x 140 cm tall, 300 kg) or DC-8 pair. One bay contains the ND:YAG and dye laser systems and LIF detection cells, and the other contains the computer used for data acquisition, laser dye, cooling water, and pumping systems.



Website: <http://cohen.cchem.berkeley.edu/>

#### *References:*

- Cleary, P.A. et al., (2002) *Applied Optics* 41(33): 6950-6956.  
Day, D.A. et al., (2002) *Journal of Geophysical Research* 107 (D6):10.1029/2001JD00077 9.  
Thornton, J.A. et al., (2000) *Analytical Chemistry* 72 (3): 528-539.  
Wooldridge, P.J. et al., (2010), *Atmospheric Measurement Techniques* 3, 593-607.