

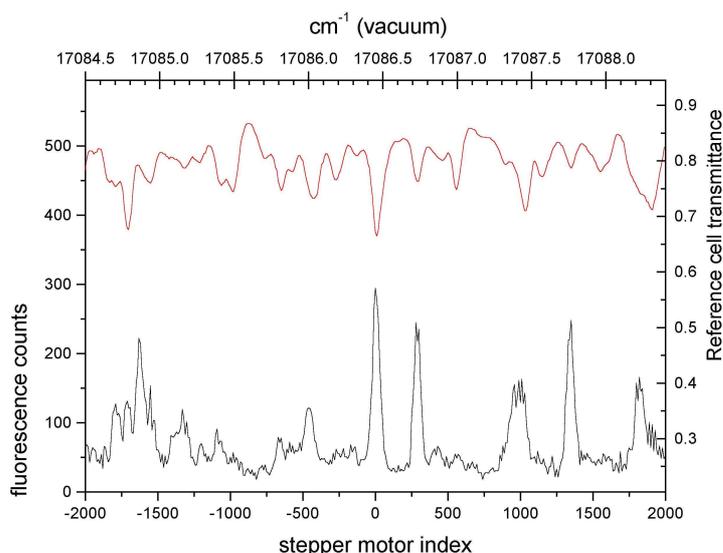
In-Situ Measurements of NO₂, ΣPNs, ΣANs, and HNO₃ by Thermal Dissociation and Laser Induced Fluorescence

Ronald C. Cohen, University of California, Berkeley

The UC Berkeley thermal-dissociation laser-induced fluorescence (TD-LIF) instrument detects NO₂ directly and detects total peroxy nitrates (ΣPNs ≡ PAN + PPN + N₂O₅ + HNO₄ . . .), total alkyl- and other thermally stable organic nitrates (ΣANs), and HNO₃ following thermal dissociation of these NO_y species to NO₂. The sensitivity for NO₂ at 1 Hz is 30 pptv (S/N=2) with a slope uncertainty of 5%. The uncertainties for the dissociated species are 10% for ΣPNs and 15% for ΣANs and HNO₃

NO₂ Detection

Briefly, the airborne TD-LIF instrument uses a compact, diode pumped, Q-switched (8 kHz, 30 nsec pulse length), frequency doubled (532nm), Nd³⁺: YAG laser to pump a tunable dye laser (100mW @ 585nm with a linewidth of 0.06 cm⁻¹) [Thornton et al., 2000]. The custom-built, etalon-tuned dye laser is used to tune the laser to excite a narrow rovibronic feature unique to NO₂. 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 colored glass are used to reject Rayleigh, Raman and chamber scatter. Single photons are counted using time-gated photon counting. The laser is alternately tuned between a strong NO₂ 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 NO₂ in the rotational state we excite [Cleary et al., 2002]. The figure illustrates the room temperature NO₂ reference cell absorption features and the jet-expansion fluorescence spectrum from scanning the laser wavelength. For sampling the stepper motor index is moved back and forth between 0 (on-line) and 200 (off-line) steps.



The gas sampled from the external probe is expanded through a 300 μm pinhole into a chamber pumped to 250 mTorr (at sea level). The rotational temperature in the expansion is estimated to be approximately 25 K, and results in a 30 fold signal enhancement. The primary instrument calibration is the response to additions of NIST traceable 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 overpressuring the inlet with zero air.

ΣPN , ΣAN and HNO_3 detection

Adding a thermal dissociation pre-reactor to the LIF detector enables the detection of ΣPNs , ΣANs and HNO_3 [Day et al., 2002; Wooldridge et al., 2010]. These species thermally dissociate to yield NO_2 and a companion radical: $\text{XNO}_2 + \text{heat} \rightarrow \text{X} + \text{NO}_2$

The sample is rapidly heated in a quartz tube, producing an enhancement in 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 NO_2 is observed. At a residence time of 30-90ms and a pressure of 1 atmosphere, approximate temperatures for complete dissociation are: 200°C for ΣPNs ; 400°C for ΣANs ; and finally 650°C for HNO_3 .

Physically, the instrument occupies 2 bays of a NASA DC-8 high rack (overall 115 x 65 x 140 cm tall, 300 kg). One bay contains the laser system and LIF detection cells and the other contains the computer, data acquisition, calibration, laser dye and cooling water, and pumping systems.



Website & References: <http://www.cchem.berkeley.edu/rccgrp/>

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