LASER-INDUCED FLUORESCENCE DETECTION OF ATMOSPHERIC NO2 AT PARTS PER TRILLION MIXING RATIOS: IMPLICATIONS FOR NITROGEN OXIDE PHOTOCHEMISTRY IN THE STRATOSPHERE AND TROPOSPHERE

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The NO2 radical affects the abundance of O3 and OH throughout the atmosphere, exerting important influence over the oxidative capacity of the atmosphere, on the distribution of compounds that contribute to the Earth's greenhouse effect, on production of organic and inorganic aerosol and on production of photochemical smog. NO2 mixing ratios vary from 10s of parts per billion (ppb) in cities to below 10 parts per trillion (ppt) in remote regions of the atmosphere. We describe a sensitive (20ppt/10 sec, S/N=2) laser-induced fluorescence (LIF) instrument designed for accurate (±5%, 1σ), continuous, autonomous, in situ observations of NO2 in any of these environs. The technique is advantageous because it is direct, in that it does not require conversion of NO2 into another species (e.g. NO) prior to detection eliminating a class of potential interferences, and it is spectroscopically specific. The instrument weighs about 200lbs including all components necessary for operation (computers, calibration gases,. . .) and consumes about 2kW of electrical power. Performance of the instrument is illustrated with 15 weeks (July-Oct 1998) of nearly continuous observations at the University of California, Blodgett Forest field station located in the foothills of the Sierra Nevada. Ambient concentrations of NO2 at this site varied from below 50 ppt to 4000 ppt and NO2 ranged from 0.05 to 0.5 of total reactive nitrogen. Analysis of these observations and related NO, NOy and O3 measurements are used to calculate regional and local scale O3 production rates. Analysis of observations obtained using our technique from NASA's ER-2 aircraft are used to infer quantitative uncertainties in reaction rate constants directly from stratospheric observations.