Upper tropospheric nitrogen oxides measured by solar absorption spectrometry

B. Sen, F.W. Irion, R.J. Salawitch, and G.C. Toon

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

1. Abstract

We report measurements of nitrogen oxide species (NO, NO_2, and HNO_3) in the mid-latitude upper troposphere (8-13 km) from the balloon-borne MkIV and the shuttle-borne ATMOS FTIR spectrometers. The FTIR spectrometers simultaneously measure the vmr profiles of a large number of gases in the upper troposphere (e.g. H_2O, O_3, CO, NO, NO_2, HNO_3, C_2H_6, etc.) using the solar occultation technique. The measured nitrogen species allows us to determine the upper tropospheric NO_x/NO_y ratio (NO_x = NO + NO_2 and NO_y = NO_x + HNO_3) and, along with measured CO, allow a broad characterization (i.e. polluted and clean) of the sampled air masses.

1.1 Areas of high confidence

MkIV measurements in the upper troposphere were obtained during four mid-latitude (35° N) balloon flights between 1990 and 1996 and the ATMOS measurements (30-50° N) are from the shuttle-borne 1994 ATLAS-III mission. The measured CO in the upper troposphere is less than 100 ppbv and had low variability between different occultations. In general no clear correlation is observed between NO_y and CO for values of NO_y smaller than 500 pptv. However, for larger values of NO_y (>500 pptv) a negative trend can be gleaned from the ATMOS/ATLAS-III measurements. The measured NO_x values are mostly less than 250 pptv at all values of NO_y and no discernible correlation is observed between NO_x and NO_y for small values of NO_y. The majority of mid-latitude air masses exhibit a NO_x/NO_y ratio less than 0.6. All of these results suggest the influence of anthropogenic pollution on the MkIV and ATMOS measurements is small. It will be shown that this behavior of NO_x, NO_y and CO is consistent with *in situ* measurements in the free troposphere.

1.2 Knowledge gaps

The MkIV and ATMOS mid-latitude upper tropospheric nitrogen oxide measurements are sparse and in regions free of anthropogenic pollution. However, airborne-measurements in the upper troposphere have shown considerable variability in NO_x and CO concentrations reflecting sources from combustion effluents, lightning, and aircraft emissions. Existing measurements from MkIV and ATMOS provide knowledge of the ability to measure the concentration of nitrogen oxide species in the troposphere for a limb observation geometry (e.g. TES). In particular, we show that

the weak tropospheric absorptions of NO and NO_2 can be distinguished from their much stronger stratospheric contributions. The inherent brightness of the Sun allows greater sensitivity at high spectral resolution, and problems in the linelist are easily discernible in the MkIV atmospheric spectra. Therefore, we will discuss the impact of deficiencies and discrepancies in the molecular spectroscopic parameter at tropospheric pressures and temperatures which can limit the retrieval precision of NO_y species from future space-borne interferometers (e.g. MIPAS and TES) and radiometers (e.g. HIRDLS).

Acknowledgement
This work was funded by NASA's Upper Atmosphere Research Program. A portion of this research was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.