Comparison of Measured and Modeled NO_2 and J_{NO_2}

H. Bösch [1], C. Camy-Peyret[2], M. Chipperfield[3], R. Fitzenberger[1], H. Harder[4,5], R. Huppert[1], S. Payan[2], D. Perner[4], U. Platt[1], M. Schneider[1,6], T. Trautmann[4], and K. Pfeilsticker[1,7]

1. Institut für Umweltphysik, Universität Heidelberg, Heidelberg, Germany
2. Laboratoire de Physique Moléculaire et Applications (LPMA), Université Pierre et Marie Curie, Paris, France
3. Environment Centre, University of Leeds, Leeds, LS2 9JT, UK
4. MPI für Chemie, Mainz, Germany
5. now at Meteorology Department, Penn State University, USA
6. now at Forschungszentrum Karlsruhe, Karlsruhe, Germany
7. also at NOAA, Aeronomy Lab, Boulder Co, USA

Abstract

Stratospheric NO_2 profiles were measured using an UV/VIS DOAS Instrument (Differential Optical Absorption Spectroscopy) operated together with the LPMA Fourier transform interferometer on a balloon gondola. This pair of instruments was employed in a series of flights at high- and mid-latitudes in different seasons. NO_2 was detected in the UV, VIS (DOAS), and IR (LPMA) in direct sunlight spectra recorded at ballon ascent, descent, and during solar occultation at maximum altitude. The measured NO_2 profiles as well as the measured slant column densities (SCD) of NO_2 were compared with the calculations of the 3-D photochemical model SLIMCAT. For the balloon ascent the model slightly underestimates the measured SCDs, while for the solar occultation measurments larger discrepancies has been found. During two balloon flights, J_{NO_2} was measured with two calibrated radiometers (2π field of view). The measured J_{NO_2} was compared with the calculations of the radiative transfer (RT) model DISORT and the RT-code used in the SLIMCAT model. An excellent agreement between the model and the measurement was found for all SZAs.

1. Introduction

The NO_x-chemistry (NO, NO_2) has a crucial influence on the abundance of stratospheric ozone. NO_x participates directly in the catalytic ozone destruction and NO_2 moderates ozone loss due to other cycles. The NO_2/NO ratio is determined by the photolysis of NO_2 and the reaction of NO with O_3. Thus, an accurate knowledge of the twilight photolysis rates is necessary to accurately model the ozone loss at low Sun conditions.

Here we report on simultaneous balloon-borne measurements of the actinic flux within the wavelength range of NO_2 photodissociation and of the line of sight column densities of NO_2 (NO_2-SCDs) and the comparison with the predictions based on two radiative transfer codes and the 3D photochemical model SLIMCAT, respectively.

2. Measurements

Stratospheric NO_2 (and many other species) was measured by the DOAS UV/VIS instrument and the LPMA FTIR on board the azimuth controlled LPMA/DOAS gondola (LPMA/Laboratoire de Physique Moléculaire et Applications; DOAS/Differential Optical Absorption Spectroscopy) at León/Spain (42.6° N, 5.7° W) on Nov. 23, 1996 and Kiruna/Sweden (67.9° N, 21.1° E) on Feb. 14, 1997 [1,2,3,4].

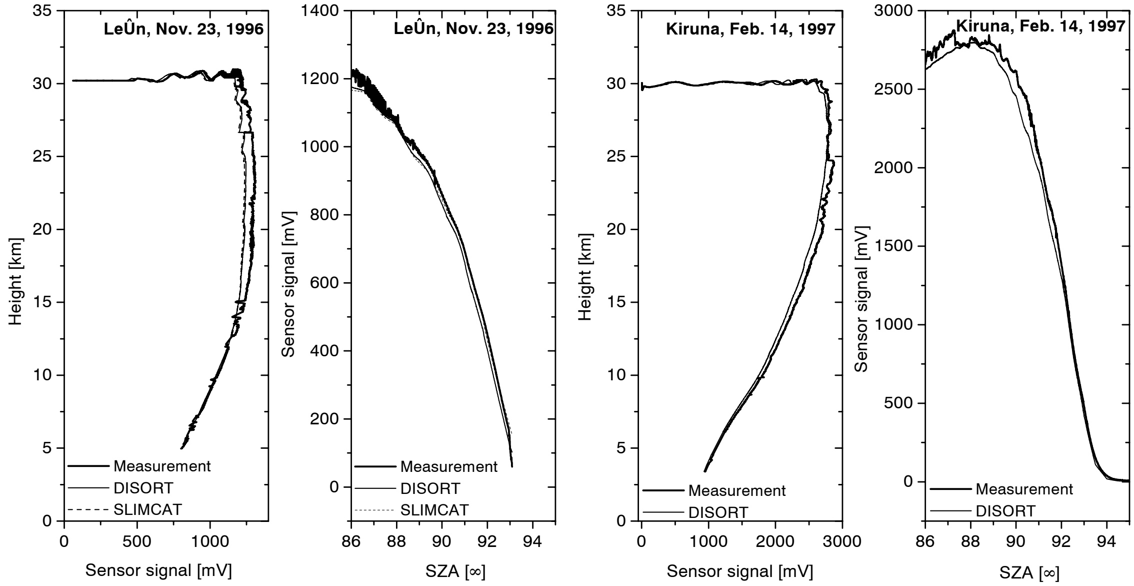

Figure 1: Comparison of the measured and the modeled sensor signal for the flight at León (left) and Kiruna (right). For the flight at Kiruna only the actinic flux calculated by DISORT is yet available.

NO_2-SCDs were determined from the measured direct Sun spectra in the UV/VIS by the DOAS technique [5]. Vertical profiles were derived from the SCDs with the matrix inversions technique and the so called onion peeling technique. For details of the LPMA retrieval see [1].

The J_{NO_2} measurements were performed with two calibrated 2π filter radiometers (similar to those described in [6]) which were mounted at the front and the backside of the gondola.

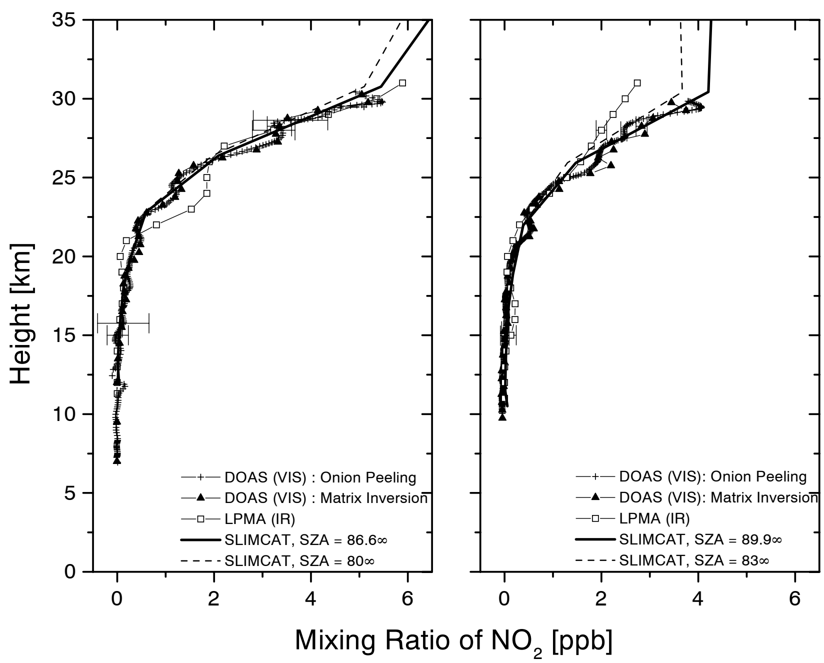

Figure 2: Comparison of the measured and the modeled NO_2 profiles for León (left) and Kiruna (right) for the balloon ascent.

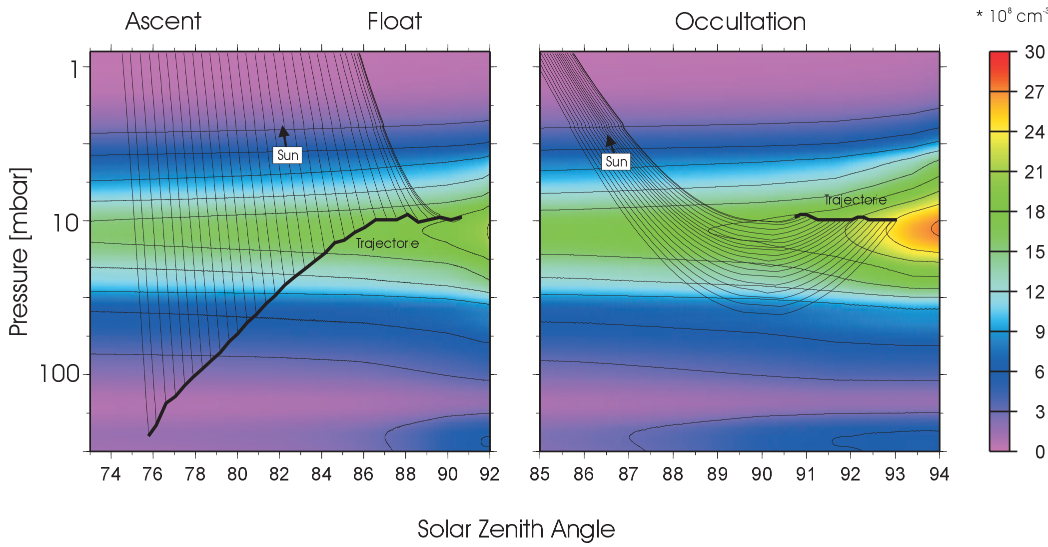

Figure 3: SLIMCAT model simulation of stratospheric NO_2 as a function of SZA and pressure for the balloon flight at León. Overlaid is the balloon trajectory and the line of sight of the measurements.

3. Model Calculations

The photochemistry of stratospheric NO_2 was calculated using a 1D photochemical model, initialized with the 12:00 local time model output of the 3D SLIMCAT UCAMB model [7]. Both models were based on the JPL-97 kinetic data. The recently updated rate constants, that determine the NO_x/NO_y partitioning were not yet included.

The RT model 1 is incorporated into the SLIMCAT model. The photolysis rates are precomputed in a look-up table for different pressures, temperatures, O_3 columns and solar zenith angles (SZA) with a scheme based on Lary and Pyle.

The RT model 2 is based on the discrete ordinate algorithm, modified to incorporate the effect of a spherical atmosphere (pseudo-spherical DISORT)[8]. The temperature, pressure and O_3 profile of nearby launched ECC-sondes was used. The aerosol extinction was inferred from SAGE II and a ground albedo of 10% and 70% was assumed for León and Kiruna, respectively.

4. Results

Fig. 1 compares the measured and the modeled sensor signals. A reasonable agreement (better than 10%) between the signals is found for all SZAs and heights.

The retrieved NO_2 profiles for both flights and the model calculations compare quite well without any photochemical corrections, except for Kiruna, where the LPMA FTIR infers smaller mixing ratios above 27 km (Fig. 2).

To account for the substantial photochemical change of NO_2 during the solar occultation measurements, modeled NO_2-SCDs were derived. The integration of the modeled NO_2 concentration along each individual line of sight yields the SCDs (Fig. 3). Due to large spatial variabilities of the NO_2 concentration (Arctic vortex) for the flight at Kiruna, the calculation of the SCDs is difficult and not shown here.

The comparison of the measured and the modeled NO_2-SCDs for León is shown in Fig. 4. For the balloon float the modeled and measured SCDs are in a good agreement. For the

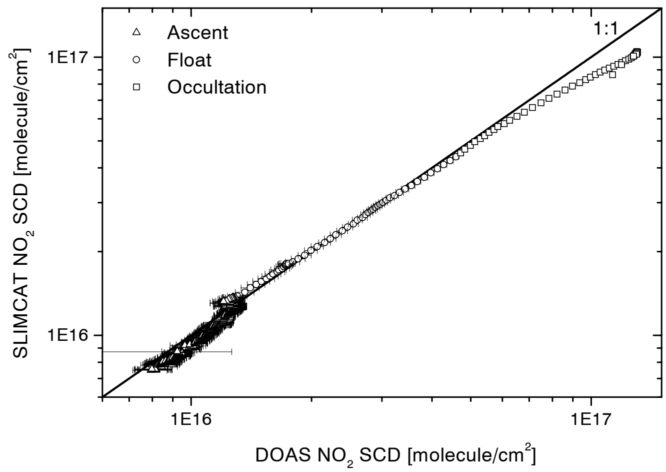

Figure 4: Comparison of the measured and the along the line of sight integrated SCDs of NO_2 for the flight at León.

balloon ascent the model slightly underestimates the measured SCDs and for solar occultation a larger discrepancy between the model calculations and the measurements is found.

5. Conclusion

The radiometric measurements of the actinic flux show that the calculations of the pseudo-spherical DISORT and the RT-code used in the SLIMCAT model are reliable for all SZAs, suggesting that the J-values in the SLIMCAT model are reasonably accurate, even for twilight conditions. The measured and modeled NO_2-SCDs were compared and discernible discrepancies were found, especially for solar occultation. An update of the rate constants of the SLIMCAT model, will probably improve the model agreement, a matter that will be subject of further investigations.

Acknowledgments / References

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