A SCIENTIFIC NO2 PRODUCT FROM SCIAMACHY: FIRST RESULTS AND VALIDATION

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ABSTRACT

A scientific NO_2 retrieval developed at the University of Bremen was applied to all available SCIAMACHY nadir spectra from August 2002 to May 2004. The NO_2 columns show the expected seasonal, latitudinal and regional variations and a good internal consistency. The precision of the individual measurements was assessed by analyzing the scatter of the results within certain areas and an excellent standard deviation of below $3x10^{14}$ molec cm^{-2} was found. Comparison of the SCIAMACHY columns with measurements from the German DOAS and FTS validation network shows very good agreement with the exception of high latitudes in summer, where a systematic under-estimation is apparent and polluted sites, where the different sensitivity of the measurement systems to tropospheric absorptions plays a role.

1. INTRODUCTION

NO_2 is an important trace gas in both the troposphere and stratosphere. It is involved in catalytic ozone depletion in the stratosphere but also reacts with halogen oxides to form reservoir substances and thereby reduces the ozone depletion potential of Cl and Br. In the troposphere, NO_2 is a key substance in ozone formation and largely emitted by anthropogenic activities.

Measurements of NO_2 can be performed either by in-situ chemical methods (mainly for air pollution monitoring or on airborne or balloon platforms) or by remote sensing in the UV/visible and IR spectral region. The latter methods can also be applied from satellite instruments, which provide global measurements of stratospheric NO_2 profiles and total column amounts.

Here, nadir measurements from the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) instrument have been analysed for NO_2, and the results been compared with those from ground-based UV/visible DOAS and FTIR instruments. As there is not yet a reliable operational NO_2 product available, SCIAMACHY spectra were analysed using a scientific DOAS algorithm developed at the University of Bremen for the analysis of GOME data. As the algorithm is very similar to that implemented in the operational processor, it is expected that the findings of this study will eventually be applicable to the operational data as well.

2. INSTRUMENT

SCIAMACHY is a 8 channel UV/visible/NIR grating spectrometer covering the wavelength region of 220 to 2400 with 0.2 – 1.5 nm spectral resolution depending on wavelength [1]. Along one orbit, the instrument performs alternating nadir and limb measurements, facilitating profile retrievals from the Mesosphere to the UT/LS region and also column measurements. In addition, solar and lunar occultation measurements are performed under certain conditions, as well as a solar irradiance measurement once per day. The UV/vis nadir measurements of SCIAMACHY are very similar to those performed by GOME, the main difference being the better spatial resolution (30x30 to 30x240 km^2) as compared to 40x320 km^2 for GOME. Global coverage at the equator is achieved in 6 days and more frequently at higher latitudes.
SCIAMACHY was launched on ENVISAT into a sun-synchronous orbit with a 10:00 LT equator crossing time (descending node) on March 1st, 2002, and nadir data are available since August of that year.

3. DATA ANALYSIS

3.1 Spectral Analysis

The data analysis is based on the well known Differential Optical Absorption Spectroscopy (DOAS) [2,3,4]. In analogy to the GOME retrieval, the wavelength window 425 - 450 nm in channel 3 was chosen for the fit. Details of the DOAS settings used are summarised in Tab. 1. A more detailed description of the NO_2 DOAS fit can be found in [4].

As the number of calibrated orbits available is limited at the time of writing, uncalibrated (lv0) SCIAMACHY spectra have been used as input for the DOAS analysis. Dark current correction was done using measurements performed on the dark side of the same orbit if possible and with the pre-flight dark current model elsewhere. The wavelength calibration is based the calibration coefficients determined before launch and a cross-calibration with an external Fraunhofer atlas [5] in the fit. Where additional orbits were distributed in lv1 format, they were used with all calibration settings with exception of dark current correction set to off to ensure consistency.

3.2 Solar Irradiance Measurements

For the solar irradiance measurements which are used as an absorption free background spectrum, two options are available for the SCIAMACHY instrument: The measurements performed with the diffuser on the Elevation Scan Mirror (ESM) and those with the second diffuser on the Azimuth Scan Mirror (ASM). Although the ESM diffuser is the default diffuser, results from the on-ground calibration measurements indicated that the ESM introduces spectral features into the measurements, and therefore a second diffuser was added to the instrument shortly before launch. As a result of the late addition, the ASM measurements are not well calibrated and not suitable for absolute radiometric measurements. However, for the DOAS fit it turned out that they yield significantly lower residuals and are therefore to be preferred. An analysis of a long time series of ASM solar measurements also revealed that with the exception of periods with heater switch offs, the instrument and diffuser appear to be very stable, and the very first ASM diffuser spectrum taken on December 15th, 2002 can be used for the analysis of the complete data set. This is in contrast to the experience with the GOME experiment [Richter and Burrows, Richter et al., 2004] and facilitates absolute measurements in the tropics as discussed below.
Based on the results of an initial validation, a constant offset of 1x10^{15} molec cm^{-2} is added to all slant columns. The reasons for this offset are not yet clear, and investigations are under way to understand and resolve this problem.

Table 1 DOAS analysis settings

Fitting window	**425 - 450 nm**
O_3	**223 K, Bogumil et al., 2003 [7]**
O_4	**298 K Greenblatt et al., 1990 [8]**
NO_2	**223 K, Bogumil et al., 2003 [7]**
H_2O	**HITRAN 2000 [9]**
Ring	**Vountas et al. [10]**
Offset	**constant**
Polynomial	**quadratic**
Wavelength cal	**Kurucz et al. [5]**

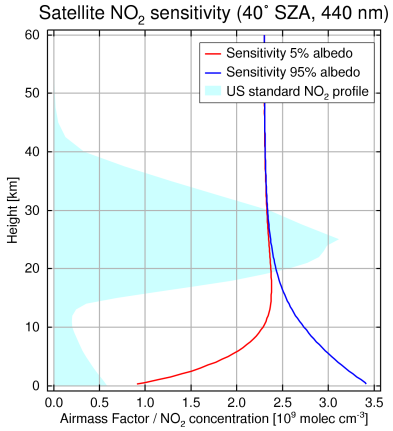

Fig. 1: Vertical sensitivity of the SCIAMACHY nadir NO_2 measurements at 440 nm, 40° SZA for low (5%) and high (95%) albedo. The US standard atmosphere NO_2 concentrations are also indicated to highlight the relative contribution of different altitude regions.

3.3 Airmass Factors

The result of the DOAS retrieval are slant column densities (SCD) integrated along the effective light path through the atmosphere. To convert these into a vertical column density (VCD), an airmass factor (AMF) is applied that corrects for the light path enhancement. The AMF are a function of solar zenith angle, the instrument line of sight, the relative azimuth between viewing direction and the sun, but also depends on atmospheric factors such as the vertical profiles of T, p, and NO_2 and parameters such as surface albedo and aerosol loading. In Figure 1, the AMF is shown as a function of altitude for two cases: low albedo (5%) and high albedo (95%). As can be seen, the differences are small in the stratosphere but large close to the surface. The same is true for the dependence on the vertical distribution, which is small above 10 km but large close to the surface and also for the impact of tropospheric aerosols. Thus, accurate determination of the total NO_2 column depends heavily on a priori assumptions that are not available from the measurements and therefore introduce uncertainties and possible biases. As an alternative approach, the target quantity in this study is the stratospheric column. To get a good estimate of this quantity, a purely stratospheric AMF is calculated with the radiative transfer model SCIATRAN [11] based on the US standard atmosphere after removing the tropospheric part and assuming a surface albedo of 5%. With this AMF, accurate results are expected for clean regions but a substantial overestimation of the stratospheric column in polluted regions. At the same time, the total column will be slightly underestimated in clean regions but very much underestimated in polluted regions. This needs to be kept in mind when interpreting the validation results discussed in Section 6.

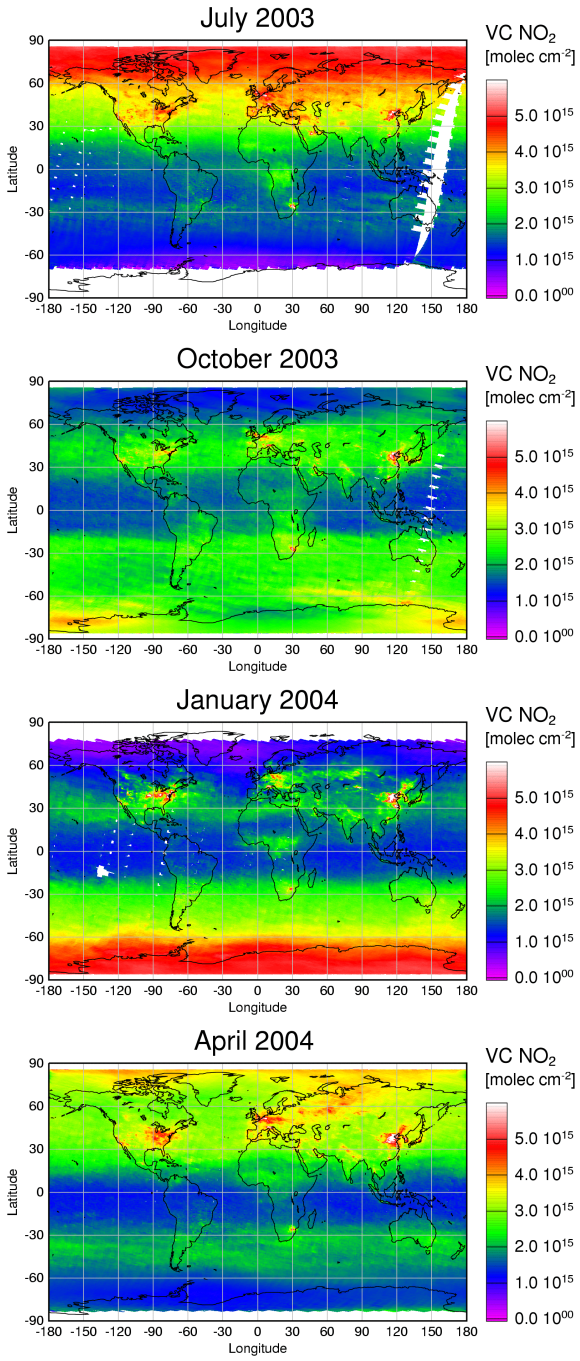

Fig. 2: Monthly averages of SCIAMACHY NO_2

4. FIRST RESULTS

To give an impression of the SCIAMACHY NO_2 columns retrieved, averages for 4 representative months are shown in Fig. 2. White gaps result from data that have not yet been provided by ESA (but will eventually be available). As a result of these missing orbits, the averages might not be fully representative in all regions. The images show that SCIAMACHY picks up all the expected features: low and more or less constant columns in the tropics, very low columns in winter in high latitudes, high columns in summer in high latitudes and seasonal varying intermediate columns in mid-latitudes. In October, the effect of the inhomogeneities from the dissolving polar vortex can be observed. Over industrialised regions and areas with intense biomass burning, the impact of tropospheric pollution is also evident.

5. ERROR ASSESSMENT

Errors can be introduced into the final columns on several levels: the spectra, the fit, and the airmass factors. Here, a detailed error discussion can not yet be given, but the precision of the data has been assessed by analysing the variability of the results in well defined areas assuming that the stratospheric column is constant and all variations in the measurements are due to measurement errors.

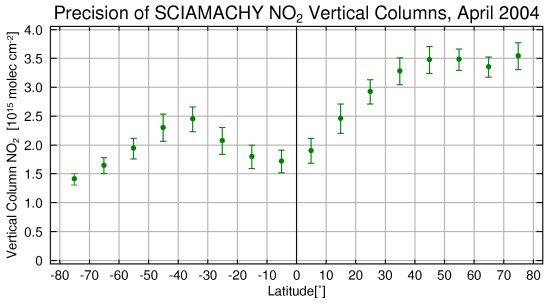

Fig. 3: Average values and standard deviation of 10° latitude bands of SCIAMACHY NO_2 in April 2004. The standard deviation can be used as an upper limited of the statistical error of the measurements.

All data from April 2004 were analysed over the clean Pacific region (180°E) in 10° latitude bands and the standard deviation was determined. Under the assumption that the NO_2 column in this region is determined by the stratospheric column, and that it is constant over +/- 5° latitude, this is a measure of the precision of the individual measurements.
The precision is determined by the amount of available light (photon shot noise) and the magnitude of the absorption which in turn is determined by the amount of NO_2 present and the light path enhancement. As can be seen from Fig. 3, the standard deviation is between $1x10^{14}$ and $2x10^{14}$ molec cm^{-2} at all latitudes, which translates into relative errors of 5-10% for individual measurements for this time period. This is an excellent precision and can be further improved by averaging over time or space. It has however to be noted, that this assessment does not include biases or other systematic errors which will have to be evaluated in further studies.

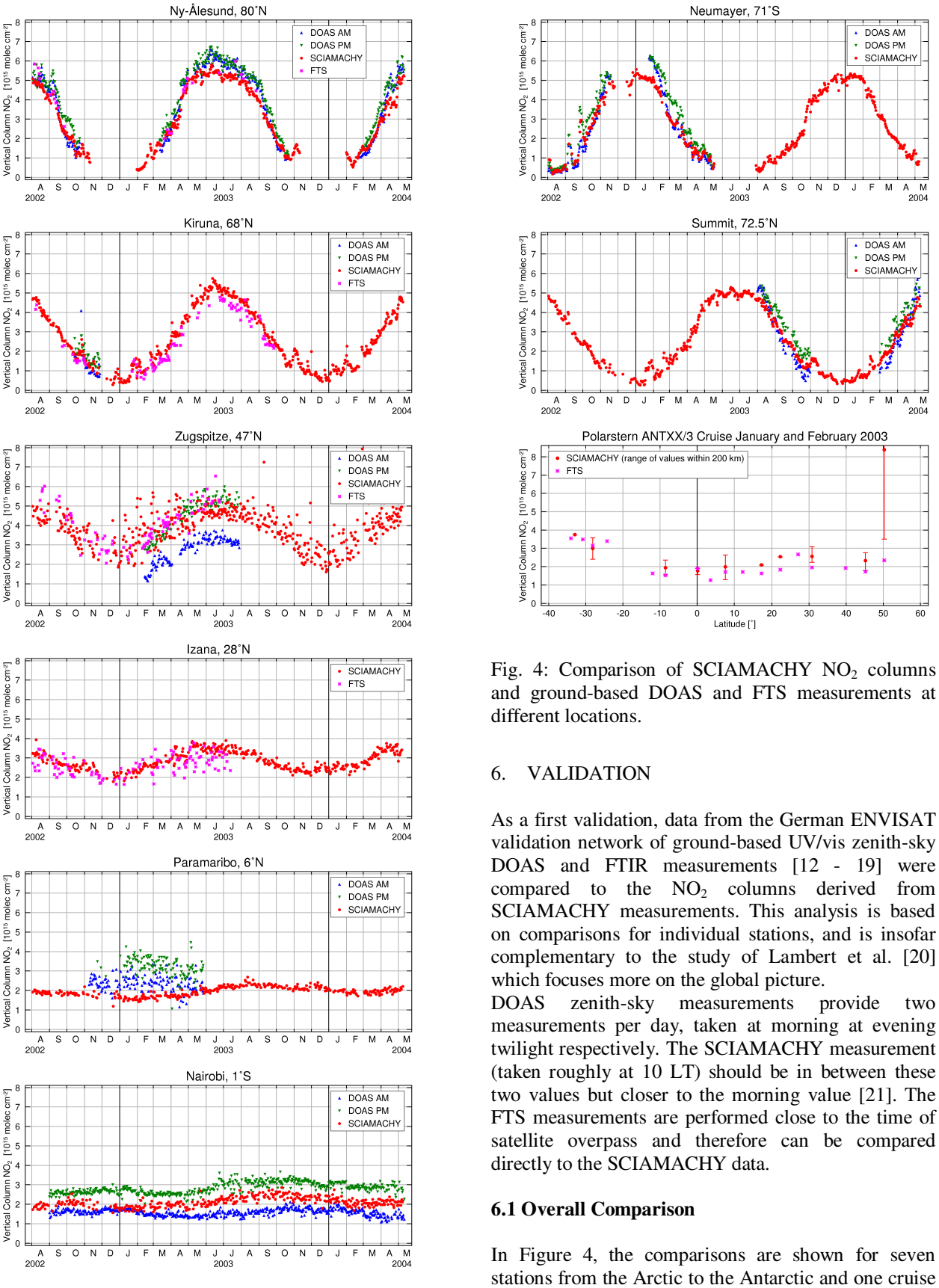

Fig. 4: Comparison of SCIAMACHY NO_2 columns and ground-based DOAS and FTS measurements at different locations.

6. VALIDATION

As a first validation, data from the German ENVISAT validation network of ground-based UV/vis zenith-sky DOAS and FTIR measurements [12 - 19] were compared to the NO_2 columns derived from SCIAMACHY measurements. This analysis is based on comparisons for individual stations, and is insofar complementary to the study of Lambert et al. [20] which focuses more on the global picture.

DOAS zenith-sky measurements provide two measurements per day, taken at morning at evening twilight respectively. The SCIAMACHY measurement (taken roughly at 10 LT) should be in between these two values but closer to the morning value [21]. The FTS measurements are performed close to the time of satellite overpass and therefore can be compared directly to the SCIAMACHY data.

6.1 Overall Comparison

In Figure 4, the comparisons are shown for seven stations from the Arctic to the Antarctic and one cruise of the Polarstern research vessel. All SCIAMACHY

measurements within 500 km were averaged to increase the number of coincidences. From the figure, the low scatter of the SCIAMACHY data is apparent and the excellent agreement for the seasonal and latitudinal variation. Also, even relatively small variations in NO_2 columns are well reproduced by the satellite measurements, even in the tropics where measurement conditions are not favourable. There is however also evidence for a slight overestimation at low latitudes (at least in Nairobi) and a clear underestimation at high latitudes in summer. It should also be repeated that an offset of $1x10^{15}$ molec cm^{-2} was added to the slant columns which translates into an offset of 0.05 - $0.5x10^{15}$ molec cm^{-2} in the vertical columns. These two points need further analysis and will have to be resolved.

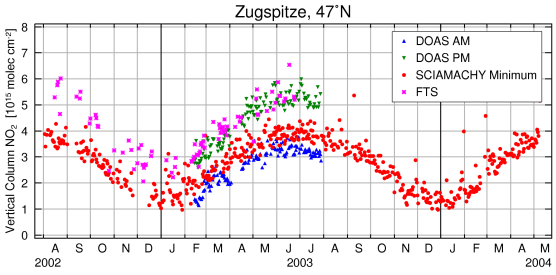

Fig. 5: Ground-based measurements at the Zugspitze compared to the smallest SCIAMACHY NO_2 column within a 500 km radius around the measurement location

6.2 Impact of Tropospheric Pollution:

As already mentioned in the data analysis section, tropospheric contributions to the signal will have an impact on the accuracy of the SCIAMACHY columns. Also, NO_2 in the lower atmosphere contributes to the columns measured by the different instruments in different ways:

- DOAS observations at twilight are relatively insensitive to tropospheric pollution as a result of the large light path enhancement in the stratosphere.
- FTS occultation measurements have a similar sensitivity to troposphere and stratosphere.
- the satellite measurement sensitivity depends strongly on the altitude of the tropospheric NO_2 and also on surface albedo and aerosol loading.

Consequently, the agreement between satellite and ground-based measurements is less good in polluted regions, for example the Zugspitze, Paramaribo or the last Polarstern measurement close to Bremen, Germany. Part of the deviations seen for example at the Zugspitze station (compare Fig. 4) can be explained by the different sensitivities of the instruments: SCIAMACHY data are influenced by boundary layer pollution in the surrounding of the station, DOAS measurements see mainly the stratosphere, and the FTS is sensitive to tropospheric pollution lifted above the station. If the satellite data are selected for the lowest value observed around the station on that day, the agreement between satellite and ground-based measurements is improved (Fig. 5). However, such a selection will always introduce a low bias.

7. SUMMARY AND CONCLUSIONS

SCIAMACHY spectra have been analysed for NO_2 absorptions using a simple DOAS algorithm developed at the University of Bremen for the GOME data retrieval. The resulting NO_2 vertical columns show small scatter and good internal consistency with respect to seasonal, latitudinal and spatial variability. The data were compared to zenith-sky DOAS and FTIR measurements from seven ground-based stations of the German ENVISAT validation network and data from a Polarstern cruise. The comparison shows excellent agreement in the seasonal and latitudinal variation, and highlights the high precision of the SCIAMACHY NO_2 data product. There is however clear indication for a low bias in high latitudes in summer, and this needs further improvement.
Although the results shown here are not based on data from the operational SCIAMACHY data processor, the algorithms and settings used are very similar, and it is expected, that eventually the operational data will be of comparable quality as the preliminary scientific products presented here.

8. ACKNOWLEGEMENTS

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9. REFERENCES

1. Bovensmann, H et al.: SCIAMACHY - Mission objectives and measurement modes, *J. Atmos. Sci.*, 56, (2), 127-150, 1999
2. Platt, U., Differential optical absorption spectroscopy (DOAS), 1994: in *Air Monitoring by Spectroscopic Techniques, Chem. Anal. Ser.*, vol. 127, edited by M. W. Sigrist, pp. 27–84, John Wiley, New York
3. Burrows, J. P., et al., The Global Ozone Monitoring Experiment (GOME): Mission Concept and First Scientific Results, *J. Atmos. Sci.*, 56, 151–175, 1999a.

4. Richter, A., and J. P. Burrows, Retrieval of Tropospheric NO_2 from GOME Measurements, *Adv. Space Res.*, 29(11), 1673-1683, 2002.
5. Kurucz, R. L., I. Furenlid, J. Brault, and L. Testerman, Solar flux atlas from 296 nm to 1300 nm, Natl. Sol. Obs. Atlas 1, 239 pp., Harvard Univ.,Cambridge, Mass., 1984.
6. Richter, A., et al: GOME observations of stratospheric trace gas distributions during the splitting vortex event in the Antarctic winter 2002 Part I: Measurements, *J. Atmos. Sci.*, in press, 2004.
7. Bogumil, K., J. Orphal, T. Homann, S. Voigt, P. Spietz, O.C. Fleischmann, A. Vogel, M. Hartmann, H. Kromminga, H. Bovensmann, J. Frerick, and J.P. Burrows, Measurements of molecular absorption spectra with the SCIAMACHY pre-flight model: instrument characterization and reference data for atmospheric remote-sensing in the 230 - 2380 nm region, *Journal of Photochemistry and Photobiology, A*, **157**, 167 - 184, 2003
8. Greenblatt, G. D., J. J. Orlando, J. B. Burkholder, and A. R. Ravishankara, Absorption measurements of oxygen between 330 and 1140 nm, *J. Geophys. Res.*, 95, 18577–18582, 1990.
9. Rothman, L. S., et al., The HITRAN molecular database editions 1991 and 1992, *J. Quant. Spectrosc. Radiat. Transfer*,48, 469–507, 1992.
10. Vountas, M., V. V. Rozanov, and J. P. Burrows, Ring effect: Impact of rotational Raman scattering on radiative transfer in earth's atmosphere, *J. Quant. Spectrosc. Radiat. Transfer*, 60, 943–961, 1998
11. Rozanov, V., D. Diebel, R. J. D. Spurr, and J. P. Burrows, GOMETRAN: A radiative transfer model for the satellite project GOME - the plane parallel version, *J. Geophys. Res.*, 102, 16683–16696, 1997.
12. Blumenstock, Th. et al.: Time Series of HNO3 Column Amounts Measured by Ground-Based FTIR Spectroscopy at Kiruna (Sweden) in Winter 1995/96 and 1996/97,Proceedings of the Fourth European Workshop on Polar Stratospheric Ozone, Schliersee 1997, European Commission - Air pollution research report 66, 411 - 414, 1998.
13. Friess, U., et al: Ground-based DOAS measurements of stratospheric trace gases at two Antarctic stations during the 2002 ozone hole period, *J. Atmos. Sci.*, in press, 2004.
14. Notholt, J. et al.: Latitudinal variations of trace gas concentrations in the free troposphere measured by solar absorption spectroscopy during a ship cruise, *J. Geophys. Res.*, 105, 1337-1349, 2000.
15. Notholt, J., et al.: Seasonal variations of atmospheric trace gases in high Arctic at 79°N, *J. Geophys. Res.*, 102, 12,855-12,861, 1997.
16. Richter, A., et al., SCIAMACHY validation using ground-based DOAS measurements of the University of Bremen BREDOM network, in *Proc. ENVISAT Validation Workshop, Frascati, 9-13 Dec. 2002*, ESA SP-531, 2003.
17. Schneider, M.: Continuous Observations of Atmospheric Trace Gases by Ground-based FTIR Spectroscopy at Izana Observatory, Tenerife Island, PhD thesis, University of Karlsruhe, FZKA Report 6727, Forschungszentrum Karlsruhe, 2002.
18. Sussmann, R., et al., Infrared spectroscopy of tropospheric trace gases: combined analysis of horizontal and vertical column abundances, *Appl. Opt.*, 36, 735-741, 1997.
19. Wittrock, F., et al.: MAX-DOAS measurements of atmospheric trace gases in Ny-Ålesund, *Atmos. Chem. Phys. Discuss.*, 3, 6109-6145, 2003.
20. Lambert et al., Geophysical Validation of SCIAMACHY NO_2 Vertical columns: Overview of Early 2004 Results, *this issue,* 2004
21. Lambert, J.-C., Investigation of Pole-to-Pole Performances of Spaceborne Atmospheric Chemsitry Sensors with the NDSC, *J. Atmos. Sci.*, 56, 176-193, 1999.