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CONSISTENT INTERPRETATION OF GROUND BASED AND GOME BrO SLANT COLUMN DATA

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ABSTRACT

Model computations of slant column densities (SCD) enable the comparison between ground based and satellite based absorption measurements of scattered light and are therefore a good basis to investigate the presence of tropospheric BrO amounts. In this study ground based zenith sky and GOME nadir measurements of BrO SCD are compared with simulations for the 19-21 March 1997 at Ny-Ålesund. The vertical columns of tropospheric BrO amounts are estimated to be in the range $4 \pm 0.8 * 10^{13}$ [molecules/cm^2] for the investigated period and location.

INTRODUCTION

The importance of the bromine species regarding the ozone depletion in polar regions and mid-latitudes has been discussed in many publications in the last years, e.g. (Chipperfield and Pyle, 1998). Approximately 40 percent of the arctic O3-depletion is due to catalytic cycles in which bromine species are involved. More over, bromine plays an important role in the tropospheric O3 "decomposition".

Model computations of Slant Column Densities (SCD), which are the integrated concentrations along the light-paths, enable the comparison between ground based and satellite based absorption measurements in zenith sky and nadir viewing geometry, respectively. They are therefore a good basis to investigate the presence of tropospheric BrO amounts, because satellite based measurements are very sensitive to tropospheric BrO amounts and ground based measurements yield information about the vertical distribution of BrO, by what it is possible (using a slant column model) to decide whether the BrO is located in the troposphere or in the stratosphere. This will be discussed in more detail in the following sections.

The knowledge of tropospheric BrO amounts is in turn useful for an appropriate interpretation of stratospheric bromine chemistry using ground based BrO slant column data, as will be discussed in more detail in section ´´Discussion´´. In this sense the synergetic use of the information from satellite based (GOME) and ground based SCD data is very important for the estimation of tropospheric portions and the interpretation of stratospheric bromine chemistry.

In the following sections we discuss the comparison of model calculations with ground based and satellite measurements (GOME) at Ny-Ålesund (79N,12E) in mid-march 1997 (19–21.03.1997). This period was chosen because of the clear sky conditions.

MEASUREMENTS

The details of the measurements as well as the ground based and satellite based instrument setups are described elsewhere (Richter et al., 1999) and (Burrows et al., 1999), here a brief description is given.

The Global Ozone Monitoring Experiment (GOME) was successfully launched on board of the European Space Agency's (ESA) second Earth Remote Sensing Satellite (ERS-2) on the 21st of April 1995. GOME provides absorption spectra of scattered sunlight, detected in nadir viewing geometry, in the wavelength range of 240 - 790 nm with a spectral resolution of 0.2 - 0.4 nm. The main scientific objective of the GOME mission is the monitoring of global total ozone distributions. Other important atmospheric trace gases, e.g. NO2, OClO and BrO, can be detected as well.

The ground based instrument was set up at Ny-Ålesund, Spitsbergen, Norway in February 1995. Absorption

spectra in the UV/visible are detected in zenith sky viewing geometry. From these the species O3, NO2, BrO and OClO are retrieved routinely (Wittrock et al., 1996). The measurements are part of the GOME validation campaign, the SCIAMACHY project and also part of the Network for Detection of Stratospheric Change (NDSC).

For both instruments the derivation of the BrO Slant Column Densities (SCD) is based on atmospheric absorption spectra of scattered sunlight measured with a diode array spectrometer. The differential optical absorption spectroscopy (DOAS) technique is applied to evaluate the SCD in the spectral range 344.7-359 nm.

As a consequence of the method of data analysis which is applied, a reference spectrum is necessary for the evaluation of the SCD. The reference spectrum of the satellite measurements usually does not contain an absorption signal of the investigated absorber, because the detected sunlight for the reference spectrum comes directly from the sun and has not traveled through the earth's atmosphere. In contrast, the reference spectrum of the ground based measurements contains an absorption signal of the investigated absorber, because the sunlight arriving at the detector has traveled through the atmosphere. As a consequence it is possible to yield absolute SCD from GOME measurements but only differential SCD (DSCD) from ground based measurements. This is a main reason why the satellite measurements are more sensitive to tropospheric BrO amounts than the ground based measurements. The SCD of a stratospheric BrO profile increases if tropospheric portions are added. As ground based measurements provide differential slant columns (DSCD) the increased SCD evaluated at a given Solar Zenith Angle (SZA) is subtracted by the increased SCD evaluated at the reference SZA. Between 80 and 92 Degree the contribution of a given tropospheric BrO amount on the evaluated SCD decreases with increasing SZA, as a result of the decreasing path length of the light in the troposphere. For example the same amount of tropospheric BrO leads to a greater increase of the SCD at 80 than at 90 Degree SZA. As a consequence tropospheric BrO amounts have a negative contribution to the evaluated BrO DSCD, hence the more tropospheric BrO the greater the negative contribution to the DSCD at high SZA.

The use of space based instruments such as GOME yield important information about the global distribution of atmospheric constituents, whereas the ground based measurements yield important information about the diurnal variation of the species, and are therefore useful to test our current understanding of the atmospheric chemistry. A model makes it possible to interpret these measurements and to compare differential with absolute SCD measurements. However the comparison of measured slant column densities with model calculations is complicated by the fast diurnal variation of these molecules and the slant path geometry. The light arriving at the detector has not all traveled via the same path through the atmosphere. Additionally the BrO profile varies with solar zenith angle (SZA) and the SZA varies along the path of the light through the atmosphere.

As a consequence it is necessary to use a combination of a photochemical model with a radiative transfer model for an appropriate interpretation of SCD data. The photochemical model provides information about the variation of the species with SZA and height, whereas the radiative transfer models provide information about the light-paths and especially about the variation of the SZA along the light-paths.

THE MODEL

The slant column model SLACO was especially developed to interpret slant column measurements of short lived species such as BrO. The main parts of this model package are Bremen's atmospheric photochemical model BRAPHO (Trentmann et al., 1997) as well as the radiative transfer models SCIARAY (Kaiser et al., 1999) and CDIPI (Rozanov et al., 2001). The photochemical model provides the diurnal variation of the species, whereas the radiative transfer models provide the information about the light-paths through the atmosphere. The models of the SLACO package are briefly described below.

BRAPHO is an atmospheric photochemical box-trajectory model. It calculates the photolysis frequencies with the module PHOTOGT (Blindauer et al., 1996) , which uses the pseudo spherical version of the radiative transfer model GOMETRAN (Rozanov et al., 1996) for the calculation of the actinic flux. Novel features of PHOTOGT are the detailed treatment of the radiative transfer especially for large solar zenith angles. Heterogeneous reaction rates on liquid and frozen aerosol particles are calculated by a module developed by K. Carslaw (Carslaw et al., 1995). Handling of data-bases and integration of the differential equations is performed with the ASAD package (Carver et al., 1997). The kinetic and photochemical data used are based on the JPL recommendation (DeMoore et al., 1997) considering the update provided in JPL00 (Sander et al., 2000).

For the interpretation of SCD measured from ground based stations BRAPHO is coupled with a full spherical ray tracing model. The recent version of the radiative transfer model SCIARAY (Kaiser et al., 1999) calculates the ray paths in fully spherical geometry based on the assumption of double scattering taking into account ground reflection

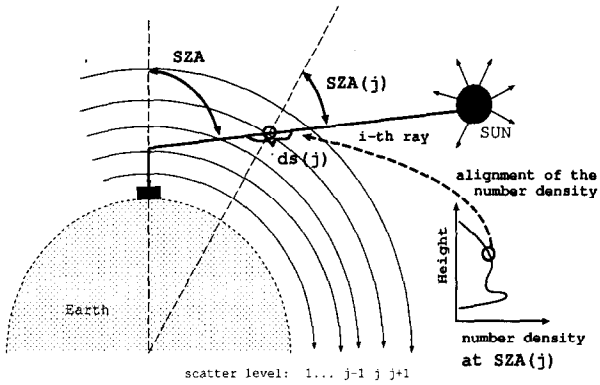

Fig. 1: Schematic illustration of the assignment of concentrations along the light-paths for the purpose of SCD calculation. ds_j = distance of the ray in the j-th scatter level, SZA_j = local solar zenith angle of the ray in the j-th scatter level.

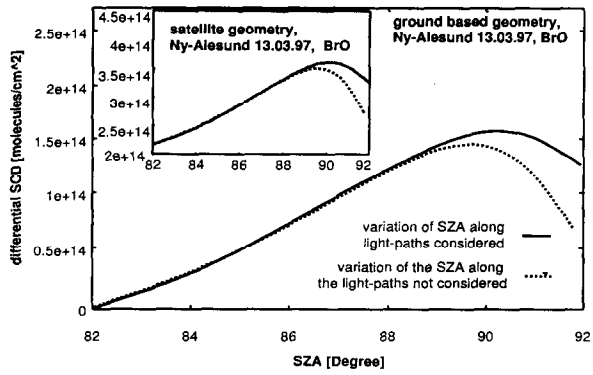

Fig. 2: The effect on the SCD, if the variation of the SZA along the light-paths is neglected for ground based and satellite geometry. The non-consideration of the SZA variation leads to significant deviations above 89 degree.

and refraction. The extinction and scattering coefficients used are calculated with GOMETRAN. For the purpose of comparison with ground based measurements the double scattering approximation is sufficient for an appropriate modeling. The underestimation of the SCD due to neglecting multiple scattering is in the range of 4 % for the simulated SCD at high SZA.

For the comparison with GOME data BRAPHO is coupled with the new fully spherical radiative transfer model CDIPI (Rozanov et al., 2001) which includes multiple scattering. Currently this model does not include refraction, but this is not critical. The GOME data discussed in this study is detected at SZA lower than 87 Degree. For this SZA refraction has no significant effect on the calculated SCD. In both cases (ground based and satellite measurements) the variation of the BrO amounts with the SZA and altitude as well as the variation of the SZA along the light path is considered. This is illustrated in figure 1. The effect on the simulated SCD if the variation of the SZA along the light-paths is neglected, is illustrated in figure 2.

ANALYSIS OF THE MEASUREMENTS

The used temperatures for the model runs was provided by the United Kingdom Meteorological Office (UKMO) (Swinbank and O'Neill, 1994). The first model runs were initialized with a pure stratospheric BrO profile, using initial BrO concentrations provided by the model SLIMCAT (Chipperfield et al., 1993). No tropospheric portions were used for this model runs. The resulting stratospheric profiles, which are based on the JPL00 chemistry, lead to a good agreement between data and simulations for ground based geometry, see figure 3 (right) and figure 5 , but a tendency to overestimate is noticeable. The same profiles lead to large discrepancies of about a factor of two for satellite SCD, see figure 3 (left).

As satellite measurements (absolute SCD) are more sensitive to tropospheric portions than ground based measurements (differential SCD), large tropospheric BrO amounts could solve the discrepancy. Similar conclusions have been drawn by other workers. For example Harder et al. (1998) reported large discrepancies between their observed stratospheric BrO vertical columns and the vertical columns estimated from the GOME data for Kiruna (68N,21E) in February 1997. They suggest that 1-2 ppt BrO uniformly distributed in the troposphere would be sufficient to solve the discrepancy.

In figure 4 the computations with additional tropospheric BrO amounts are illustrated, in each case a constant BrO background uniformly distributed in the troposphere was assumed. Good agreement between simulated and observed satellite SCD can be achieved if tropospheric amounts in the range of $4\pm0.8 * 10^{13}$ [molecules/cm^2] , or 2-3 ppt respectively, are assumed to be in the troposphere.

Model runs with these amounts of tropospheric BrO also yield good agreement between simulated and observed differential SCD for the ground based geometry. This is an important point, because it demonstrates that significant

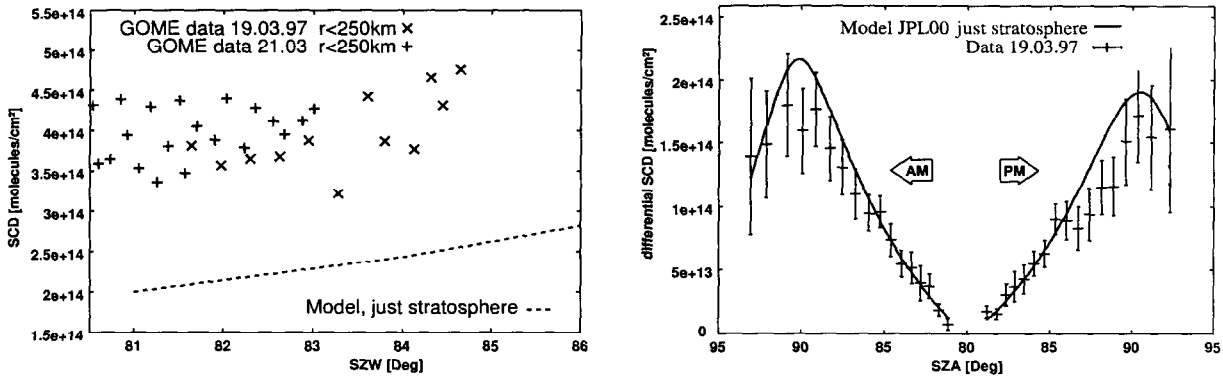

Fig. 3: Comparison of simulated SCD with observed SCD data. Left, GOME observations vs. simulations - right, ground based observations vs. simulations. Just stratospheric BrO is considered.

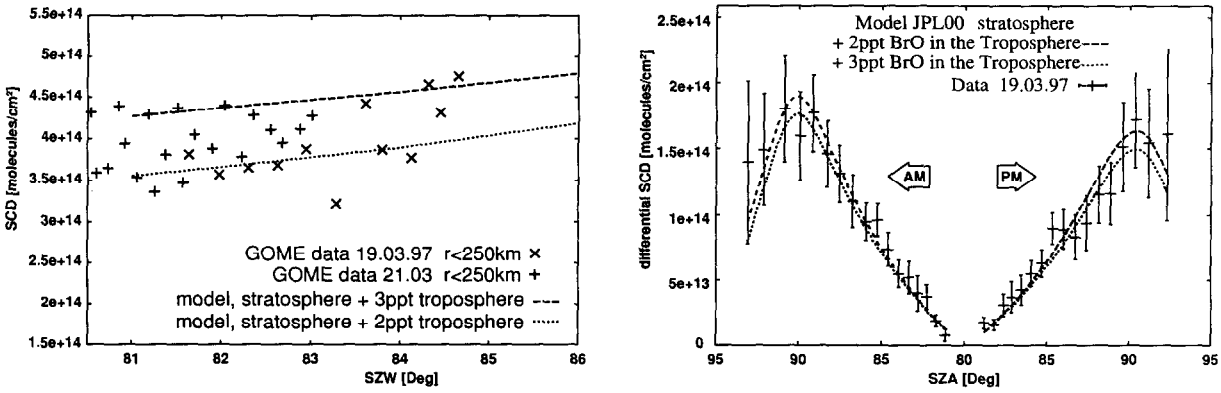

Fig. 4: Comparison of simulated SCD with SCD data for satellite based and ground based observations, with 2 pptv and 3 pptv BrO throughout the troposphere, which has been added to the stratospheric profiles.

BrO amounts are present in the troposphere. The agreement between GOME data and model calculations can also be improved if the BrO amounts in the stratosphere are increased without the consideration of tropospheric BrO, but then the agreement between ground based measurements and model calculations gets worse, because the DSCD increases. Hence a consistent interpretation is only possible if tropospheric BrO amounts are considered.

DISCUSSION

In the JPL97 update JPL00 (Sander et al., 2000) a new recommendation for the HOBr absorption cross section and the BrONO2 hydrolysis is provided, which has been used in the presented JPL00 model runs. The BrONO2 hydrolysis is very fast even at high temperatures of about 210 Kelvin. Therefore BrONO2 is transformed to HOBr via the hydrolysis reaction, especially during the night. The photolysis rate of HOBr recommended in JPL97 is slower than the photolysis rate of BrONO2 at high SZA around 90 Degree. Therefore the transformation of BrONO2 to HOBr does not lead to an enhancement of BrO in the morning using the JPL97 HOBr photolysis. But the HOBr photolysis recommended in JPL00 is at twilight (at SZA of about 90 Degree) a factor of two faster than the old one, and leads therefore to increased BrO amounts especially in the morning. The new JPL00 BrONO2 hydrolysis lets the reaction rate unchanged at temperatures of about 190-198 K, but leads to a enhancement of the reaction rate of about a factor of 2 at temperatures between 210-215 K, which are typical for March in mid-latitudes. The JPL00 BrONO2 hydrolysis enhances therefore the effect of the new HOBr photolysis at moderate temperatures (e.g. 210-215 K).

Additionally the reaction of BrONO2 with O(3p) has been implemented in the JPL00 model chemistry. This reaction leads to an enhancement of BrO at altitudes above approximately 30 km, where heterogenous reactions are not significant, but the concentration of O(3p) increases.

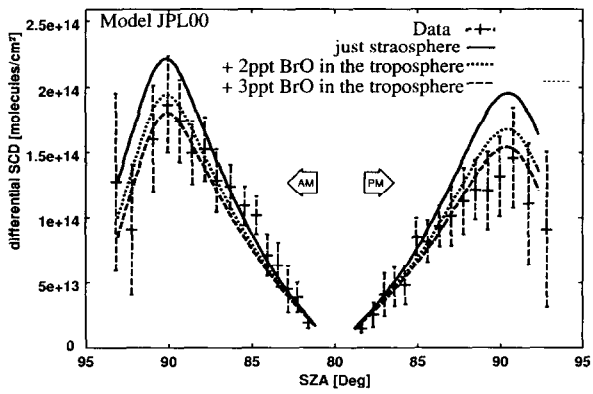

Fig. 5: Comparison of simulate SCD with SCD data for ground based observations, 21.03.97, with 2 pptv and 3 pptv BrO throughout the troposphere, JPL00 chemistry.

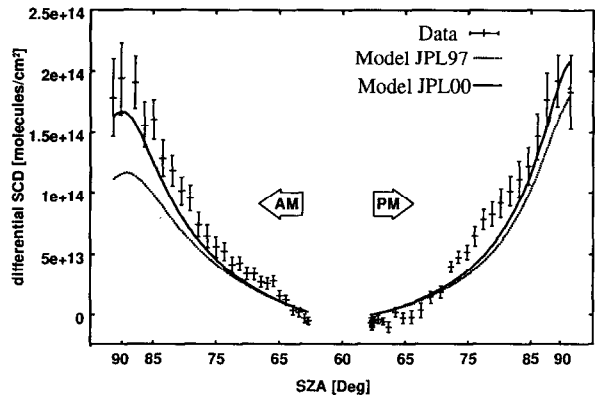

Fig. 6: Comparison of model runs with ground based DOAS data at Bremen, 53N, 04.03.97. The agreement between data and simulations gets much better if the JPL2000 chemistry is used.

With the JPL97 chemistry the agreement between ground based measurements and the model calculations is poorer, that is, if the tropospheric profiles used in this study are added to the stratospheric profiles (Mueller et al. 1999). Moreover the JPL97 chemistry leads to large discrepancies between observed and simulated SCD in mid-latitudes (Bremen, late winter) in the morning, see figure 6. On the other hand the JPL97 chemistry leads to a better agreement between simulated and observed BrO SCD at Ny-Ålesund for the investigated period than the updated JPL97 (JPL00) chemistry, if only small tropospheric BrO amounts in the range of 0.5-1 ppt are considered.

Hence a consistent interpretation of ground based and GOME data at Ny-Ålesund as well as in mid-latitudes is only possible if the JPL00 chemistry instead of the JPL97 chemistry is used and the estimated tropospheric portions (2-3 ppt) are considered. This demonstrates that comparison of simulations with satellite and ground based SCD are not only a good basis to investigate the presence of tropospheric BrO amounts, but that they are also very useful for the interpretation of stratospheric bromine chemistry.

For the estimation of the tropospheric amounts a profile with constant mixing ratio has been used. The possibility of getting profile information about tropospheric BrO from the comparison of GOME and ground based zenith sky measurements is limited by the following circumstances.

- The relatively large horizontal size of the GOME pixel (40x320 km), linked with the spread of the data.
- The relatively small sensitivity of the data on the profile shape, linked with the errors of the data.
- Few GOME data at high SZA.

The described handicaps are mainly a result of the zenith sky respectively nadir viewing geometry. Therefore other measurements and further development of tropospheric models are necessary to obtain improved quantitative information about tropospheric absorber and their profiles. With the launch of the SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric CHartographY) (Bovensmann et al., 1999) spectrometer a better global mapping of tropospheric absorber will be possible. SCIAMACHY is designed to measure absorption spectra in the wavelength region (240 nm - 2380 nm) at moderate spectral resolution (0,2 nm - 1,5 nm). A special feature of SCIAMACHY is the combined limb-nadir measurement mode and the possibility of occultation measurements, which enables the tropospheric column amounts of several trace gases to be determined. SCIAMACHY is planned to be launched in autumn 2001.

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REFERENCES

Blindauer, C., V. Rozanov, and J. P. Burrows, Actinic flux and photolysis frequency comparison computations using the model PHOTOGT, *J, Atmos. Chem.*, **24**, 1-24, 1996.

Bovensmann, H., J. P. Burrows, M. Buchwitz, J. Frerick, S. Noël, V. V. Rozanov, K. V. Chance, and A. H. P. Goede, SCIAMACHY: Mission Objectives and Measurements Modes, *Journal of Atmospheric Sciences*, **56**, 127-150, 1999

Burrows, J.P., M. Weber, M. Buchwitz, A. Rozanov, A. Ladstätter-Weißenmayer, A. Richter, R. DeBeek, R. Hoogen, K. Bramstedt, K.U. Eichmann, M. Eisinger , and D. Perner, The Global Ozone Monitoring Experiment (GOME): Mission Concept and First Scientific Results, *J. Atmos. Sci.*,**56**, 151-175, 1999.

Carslaw, K.,B. Luo, and T. Peter, An analytic expression for the composition of aqueous HNO_3- H_2SO_4 stratospheric aerosols including gas phase removal of HNO_3, *Geophys. Res. Lett.*, **22**, 1877-1880, 1995.

Carver, G., P. Brown, and O. Wild, The Asad atmospheric chemistry integration package and chemical reaction data base, *Computer Physics Communications*,**105**, 197-215,1997.

Chipperfield, M.P., D. Cariole, P. Simon, R. Ramaroson and D.J. Lary, A three dimensional modelling study of trace species in the Artic lower stratosphere during winter 1998-1999, *J. Geophys. Res.*, **98**, 7199-7218,1993

M.P. Chipperfield and J.A. Pyle, "Model sensitivity studies of Arctic ozone depletion", *Journal of Geophysical Research*, **103**, 28,389-28,403, 1998

DeMore, W., S.P. Sander, C.J. Howard, A.R. Ravishankara, D.M. Golden, C.E. Kolb, R.F. Hampson, M.J. Kurylo, and M.J. Molina, Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling, Evaluation 12, NASA JPL Publication 97-4, 1997.

H. Harder, C. Camy-Peyret, F. Ferlemann, R. Fitzenberger, T.Hawat, H. Osterkamp, M. Schneider, D. Perner, U. Platt, P. Vradelis, and K. Pfeilsticker, Stratospheric BrO profiles measured at different latitudes and seasons: Atmospheric observations, *Geophys. Res. Lett.*, **25**, 3843-3846, 1998

Kaiser J., V. Rozanov, M. Buchwitz, and J.P. Burrows, Steps Towards Limb Profile Retrieval using a Spherical Radiative Transfer Model based on the Single Scattering approximation, Proceedings of the European Symposium on Atmospheric Measurements From Space (ESAMS, ISSN 1022-6656), pp. 771-777, ESA-ESTEC, Nordwijk - The Netherlands, 1999.

Mueller R. , H. Bovensmann, M. Bruns, V. Eyring, J. Kaiser, A. Richter, J. Trentmann , F. Wittrock, and J.P. Burrows, Interpretation of BrO Slant Column Measurements using the Model Package SLACO, Proceedings of the European Symposium on Atmospheric Measurements From Space (ESAMS, ISSN 1022-6656), pp. 617-619, ESA-ESTEC, Nordwijk - The Netherlands, 1999.

A. Richter, Eisinger M., Ladstätter-Weißenmayer A., Richter A. and Burrows, J. P. , DOAS zenith-sky observations. 2. seasonal variation of BrO over Bremen (53 N) 1994-95, *Journal of Atmospheric Chemistry*, **32**, 83-99, 1999

Rozanov, V., D.Diebel, R.Spurr and J.P.Burrows, GOMETRAN: A radiative transfer model for the satellite project GOME – the plane parallel version, *J. Geophys. Res.* , **102**, 16683-16695, 1997.

Rozanov A. , V. Rozanov, and J. P. Burrows, A numerical radiative transfer model for a spherical planetary atmosphere : Combined differential–integral approach involving the Picard iterative approximation, *Journal of Quantitative Spectroscopy and Radiative Transfer*, in press

Sander S.P., W.B. DeMore, R.R. Friedl, D.M. Golden, R.F. Hampson et al., Update of key reactions of JPL97 recommendations available on the Internet, http://jpldataeval.jpl.nasa.gov/

Swinbank, R., and A. O'Neill, A stratosphere-troposphere data assimilation system, *Mon. Weather Rev.*, **122**, 686-702 , 1994

Trentmann, J., V. Eyring, H. Bovensmann, and J.P. Burrows, Influence of Refraction on Polar Photochemistry - Simulations with the New Photochemical Model BRAPHO , Proceedings of the Fourth European Symposium on Ploar Stratospheric Ozone, ISBN 92-828-2365-2, pp. 317-320, 1997

Wittrock, F., M. Eisinger, A. Ladstätter-Weißmayer, A. Richter, and J. P. Burrows: Ground based UV/VIS measurements of O3, NO2 , BrO and OClO over Ny-Ålesund (78°N), in: Polar stratospheric ozone, Air pollution research report 56, Proceedings of the 3rd European Polar Ozone Symposium, Schliersee, Germany, CEC, pp. 329-334, 1996