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First simultaneous global measurements of nighttime stratospheric NO₂ and NO₃ observed by Global Ozone Monitoring by Occultation of Stars (GOMOS)/Envisat in 2003

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[1] The Global Ozone Monitoring by Occultation of Stars (GOMOS) stellar occultation instrument on board the Envisat European satellite provides global coverage of ozone and other stratospheric species with good vertical resolution and a self-calibrating method. In this paper we present the first simultaneous global distribution of stratospheric NO₂ and NO₃ from 1 year of nighttime GOMOS data in 2003. Most previous NO₂ satellite observations have been made using the solar occultation technique. They are difficult to interpret due to the fast photochemical evolution of NO₂ at sunrise and sunset. There are no published observations of NO₃ from space because this constituent is rapidly photodissociated during daytime and is not observable by solar occultation. It is shown that the NO₂ mixing ratio reaches a maximum around 40 km with values between 14 and 16 ppbv at low and middle latitudes. The global distribution of NO₂ observed by GOMOS is very similar to the NO + NO₂ Halogen Occultation Experiment climatology deduced from sunset measurements from 1999 to 2004. At high latitude a high mixing ratio is observed in the north vortex in November 2003 after a strong solar proton event and in the south vortex in July 2003. The NO₃ mixing ratio peaks at 40–45 km. NO₃ follows a semiannual variation at low latitudes with maxima at equinoxes and an annual variation at middle and high latitudes with a maximum in summer. In the upper stratosphere the mixing ratio of NO₃ is strongly correlated with temperature due to the thermal dependence of its formation rate.

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1. Introduction

[2] Odd nitrogen species play an important role in the photochemistry of stratospheric ozone. In the middle and upper stratosphere they participate in the catalytic destruction of ozone. In the lower stratosphere they form reservoir

species like ClONO₂ which inhibit the efficiency of the catalytic destruction by halogen gases.

[3] The main source of NO₂ is the photolysis of N₂O by solar UV radiation. Other significant potential sources are the upward transport of NO₂ produced by lightning in the tropical upper troposphere and the downward transport of NO from the thermosphere or the mesosphere in the winter polar vortex.

[4] NO₂ profiles have been measured from space by several instruments. Most observations were performed using the solar occultation technique, Stratospheric Aerosol and Gas Experiment (SAGE) II [Cunnold *et al.*, 1991], Halogen Occultation Experiment (HALOE) [Gordley *et al.*, 1996], Polar Ozone and Aerosol Measurement (POAM) III [Randall *et al.*, 2002], during sunrise or sunset when the concentration is changing very quickly, which makes the interpretation very difficult. Some others were obtained from the measurement of sunlight scattering at limb during daytime, Solar Mesospheric Experiment (SME) [Mount *et al.*, 1984], Odin Spectrometer and IR Imager System

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(OSIRIS) [Storis *et al.*, 2003] and are not directly comparable with Global Ozone Monitoring by Occultation of Stars (GOMOS) due to the strong diurnal cycle of NO₂. A few nighttime observations are available for limited periods. They were obtained from the detection of the limb infrared emission by Limb Infrared Monitor of the Stratosphere (LIMS) from October 1978 to May 1979 [Russell *et al.*, 1988], Improved Stratospheric and Mesospheric Sounder (ISAMS) from September 1991 to July 1992 [Reburn *et al.*, 1996] and Cryogenic Limb Array Etalon Spectrometer (CLAES) from October 1991 to May 1993 [Danilin *et al.*, 1999]. Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) [Fischer and Oehlaf, 1996] on board Envisat is also providing such observations since July 2002. Local NO₂ profiles are also obtained by several balloon-borne instruments including stellar and moon occultation spectrometers [Renard *et al.*, 1996, 2001], a Michelson interferometer MIPAS-Balloon (MIPAS-B) [Friedl-Vallon *et al.*, 2004] and a Fourier transform interferometer Far Infrared Spectrometer (FIRS)-2 [Johnson *et al.*, 1995].

[5] NO₃ is a transition species for the transformation of NO₂ into the N₂O₅ reservoir during night. There are no published observations of NO₃ profiles because this species is rapidly photodissociated during daytime and is undetectable by solar occultation or limb scattering observation. SAGE III, launched in December 2001, has the capability to measure NO₃ in moon occultation mode but the results are not yet published. A few local profiles were obtained up to 40 km at mid and high latitudes by balloon-borne stellar and moon occultation instruments [Renard *et al.*, 1996, 2001].

[6] GOMOS, on board the European satellite Envisat launched 1 March 2002, is the first space instrument dedicated to the study of the atmosphere of the Earth by the technique of stellar occultation [Bertaux *et al.*, 2004]. When a star sets behind the atmosphere, its light is absorbed by atmospheric constituents. Each constituent can be identified by its absorption spectrum. The atmospheric transmission spectrum is equal to the ratio between the star spectrum absorbed by the atmosphere and the reference star spectrum outside the atmosphere. As the reference spectrum is measured at the beginning of each occultation, we can consider GOMOS as a self-calibrated instrument, independent of any radiometric calibration. With four spectrometers, the wavelength coverage from 248 nm to 942 nm allows monitoring ozone, H₂O, NO₂, NO₃, atmospheric density from Rayleigh extinction, aerosols, O₂ and temperature profiles from the upper troposphere to the mesosphere. Two additional fast photometers (1 kHz sampling rate) are used to correct star scintillation perturbations and to determine high vertical resolution temperature profiles.

[7] The main objective of the GOMOS/Envisat instrument is to build a very accurate global climatology of ozone and chemical species involved in ozone photochemistry. This climatology will be used to study the atmospheric natural variability, to test the validity of chemistry transport models and as a reference for future trend studies. GOMOS nighttime measurements are especially well adapted for this task due to their self-calibrating nature and the perfect knowledge of their altitude, a

particularity of the star occultation technique. The goal of this paper is to present first simultaneous global measurements from space of nighttime NO₂ and NO₃ observed by GOMOS in 2003.

2. Data Processing

[8] Results presented here are obtained using version V6.0 of the algorithms. This version has been implemented in April 2004 for the full reprocessing of 2003 data. It is not yet fully validated, especially for NO₂ and NO₃, due to the small number of available validation data in nighttime conditions. A few profiles have been compared with those of a balloon-borne moon occultation instrument in the frame of Atmospheric Chemistry Validation (ACVE2) by Renard *et al.* [2004]. They conclude that balloon and GOMOS profiles compare reasonably well on the average although GOMOS is not able to capture fine-scale vertical structures seen in balloon profiles. Further validation is needed to improve our confidence in the quality of GOMOS data. However, this kind of exercise is limited by the difficulty to find good coincidences in time and space and we consider very useful to present a full year of GOMOS NO₂ band NO₃ measurements even if they are not fully validated. Furthermore, the internal consistency of the data gives us confidence in their quality, at least for averaged profiles for which the random error is minimized. Our results will be available for comparison with those of other satellites instruments and with the outputs of chemistry transport models on a global basis.

[9] The main characteristics of the data inversion in V6.0 are summarized below. The inversion of spectrometer data from level 1b (calibrated transmission spectra) to level 2 (vertical profiles of constituents) is made in two steps, the spectral inversion and the vertical inversion.

2.1. Spectral Inversion

[10] The goal of the spectral inversion is to determine the number of molecules along the line of sight (slant densities) of each absorber from the transmission spectrum corrected from refraction effects. In the prelaunch algorithm, a global spectral inversion was made simultaneously on all retrieved species (O₃, NO₂, NO₃, aerosols with a 1/λ extinction dependence and air density) using a Levenberg-Marquardt nonlinear least square method [Press *et al.*, 1986] to fit the measured transmission by the model transmission. More details are given by Kyrölä *et al.* [2004]. This global method was also used by Yee *et al.* [2002] for the inversion of UV and visible spectra from the Midcourse Space Experiment (MSX) satellite. It worked well for ozone at all altitudes and for minor species (NO₂ and NO₃) above 40 km. Below 40 km, spectra are affected by scintillations due to small-scale atmospheric turbulent structures and vertical line density profiles of NO₂ and NO₃ exhibited often large unrealistic fluctuations. In order to solve this problem, a differential optical absorption spectroscopy (DOAS) method was implemented in V6.0 for these two species. The DOAS principle is to determine the densities of trace gases by measuring their specific narrow band absorption structures [Platt, 1994]. In our case, the differential spectrum is obtained by removing a 15 nm (30 nm) moving average respectively for NO₂ (NO₃). The temperature dependence of

NO₂ and NO₃ cross sections is taken into account using ECMWF temperatures along the line of sight.

2.2. Vertical Inversion

[11] The goal of the vertical inversion is to compute local density profiles as a function of altitude from slant density profiles as a function of tangent altitude. In the prelaunch algorithm, the vertical inversion was made using an onion peeling method with a linear interpolation between layers. This method may amplify oscillations due to noisy data and scintillations, especially in the bottom of the profiles where the altitude sampling is reduced by the refraction. In order to attenuate this effect, a Tikhonov inversion technique with a second difference smoothness constraint [Kyrölä *et al.*, 1993] is applied in V6.0 with a constant vertical resolution fixed to 4 km in the case of NO₂ and for NO₃. A similar method was used by Yee *et al.* [2002]. It is worth to note that this method does not use an a priori profile.

2.3. Data Accuracy

[12] The uncertainty on local densities includes a random part due to photon counting, detector noise and chromatic scintillation effect and a systematic part due to uncertainties in the data processing parameters (cross sections, instrument spectral resolution). The random error depends on the brightness of the star in the spectral range of strongest absorption by the retrieved species (400–450 nm for NO₂ and 630–670 nm for NO₃). These two spectral bands are not too far from 550 nm used for the definition of the visual magnitude. If we consider only the 70 brightest stars (visual magnitude < 2.25), the random error of an individual profile is not larger than 20% for NO₂ between 25 and 45 km and 30% for NO₃ between 30 and 45 km and increases to 40% at 50 km and 20 km for NO₂ and 60% at 50 km and 25 km for NO₃ and higher values above and below these altitude ranges. For this study, we limit the data analysis to 20–50 km for NO₂ and 25–50 km for NO₃. Outside these altitude ranges GOMOS data have to be considered with caution. The systematic error is more difficult to estimate. Uncertainties in cross sections and on their dependence on temperature may have a significant contribution to the error budget. Vandaele *et al.* [2002] report up to 7% differences between NO₂ cross sections measured by different groups and Orphal *et al.* [2003] mention up to 10% differences for NO₃. For the present study, we use monthly mean profile in 15° latitude bands resulting from the average of 100–500 individual profiles. The random error is reduced to only a few percent (inversely proportional to the square root of the number of profiles) and the total error budget is dominated by systematic errors which are not or less reduced by the averaging process. It can be roughly estimated to 10% for NO₂ and 15% for NO₃.

3. Data Selection and Averaging

[13] One difficulty of the stellar occultation technique is the sensitivity of the data quality to star characteristics (brightness, temperature) and to viewing geometry (sun azimuth and elevation, occultation obliquity). Furthermore, for a given star, the latitude of the tangent point depends on the day of the year and the latitude coverage changes with time. In order to build three-dimensional NO₂ and NO₃

fields as homogeneous as possible, a three-step selection and averaging procedure is applied. (1) We use only the 70 brightest stars and we discard daylight observations to eliminate too noisy NO₂ and NO₃ profiles. (2) For a given star and during 1 day, the latitude of the tangent point is almost constant and the star is occulted 14 or 15 times (once per orbit) with a 25° westward longitude shift per orbit. A daily mean profile is computed as the weighted average of all available profiles amongst the 14–15 ones. Weights are inversely proportional to the squared inverse error estimates. Each daily mean profile can be considered as a zonal average at the mean latitude of the tangent point. (3) All daily mean profiles for 1 month and within a 15° latitude band are averaged taking into account their weights as indicated in step 2.

4. Results and Discussion

4.1. NO₂

[14] Partitioning of odd nitrogen family, defined as NO + NO₂ + NO₃ + N₂O₅, is controlled in the stratosphere by the fast photochemical equilibrium between NO and NO₂ and the slow photodissociation of N₂O₅ during daytime and the slow conversion of NO₂ into NO₃ and then into N₂O₅ during nighttime. Owing to these photochemical reactions, the NO₂ concentration is never constant. It is slowly decreasing by night and increasing by day and rapidly increasing at sunset and decreasing at sunrise. It is therefore very important to take into account the local time when comparing measurements made by different instruments. In the case of GOMOS, nighttime observations are made during the ascending path of Envisat and the local time is approximately equal to the local hour of the ascending node, 1000 LT.

[15] GOMOS provides NO₂ vertical profiles in absolute concentration as a function of geometric altitude. For photochemistry studies and comparison with other measurements and models, it is more convenient to consider mixing ratios. Figure 1 shows latitude-altitude maps of NO₂ for each month in 2003 except May where very few measurements are available due to a failure in the star pointing system. Mixing ratios have been computed using European Centre for Medium-Range Weather Forecasts (ECMWF) pressure and temperature interpolated to the time and location of GOMOS measurements. At mid and low latitudes, a maximum in the vertical profile is observed around 40 km in both hemispheres. The peak value ranges from 14 to 16 ppbv depending on the month and its latitude location varies between 20°S and 20°N with a shift toward the summer/autumn hemisphere, to the south from February to April and to the north from August to November. This value is slightly smaller than the results of Reburn *et al.* [1996] who found a 17 ppbv peak of nighttime NO₂ around 3 hPa (~40 km) in ISAMS and LIMS January data at equatorial and south tropical latitudes. At high latitude, lower values are observed in general, except when a strong descent of air enriched in NO_x (NO + NO₂) of mesospheric or thermospheric origin occurs inside the winter polar vortex. It is interesting to note the strong peak of NO₂ above 38 km, with up to 38 ppbv at 50 km, in the northern high latitude upper stratosphere in November. This peak has been attributed by Seppälä *et al.* [2004] to the formation of

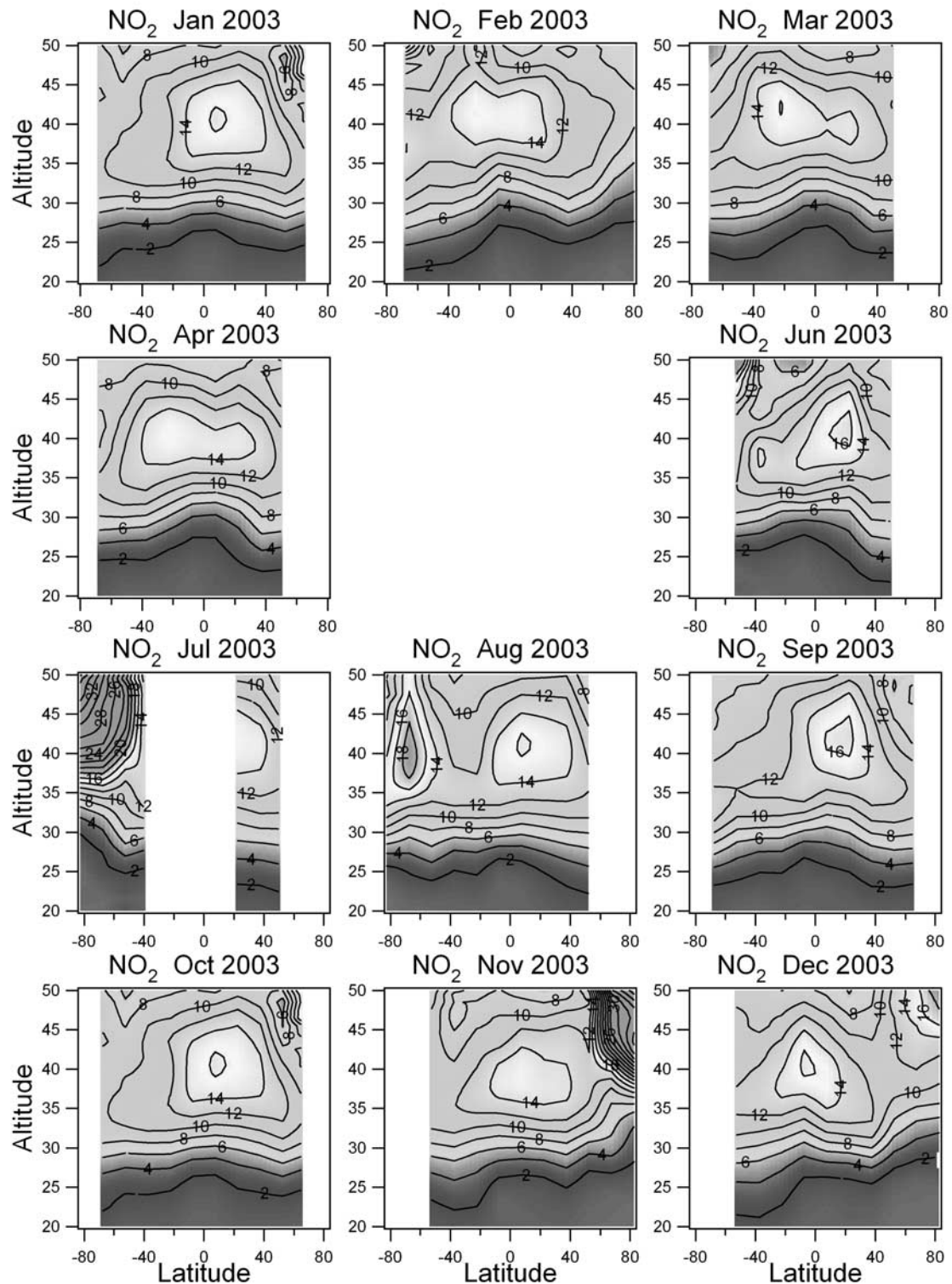


Figure 1. Latitude-altitude maps of NO₂ mixing ratio in ppbv for each month in 2003. See color version of this figure in the HTML.

a large amount of NO_x during the very intense solar proton event at the end of October 2003. Such NO₂ enhancement after strong solar proton events have been observed and simulated in the past [Jackman *et al.*, 2000, 2001; Verronen *et al.*, 2002]. A very high mixing ratio (up to 36 ppbv at

50 km) is also detected in July at southern high latitude. It is probably due to the strong diabatic descent of mesospheric and thermospheric air with high NO_x mixing ratio in the southern winter polar vortex and a contribution of two moderate solar proton events occurring on 28–30 May and

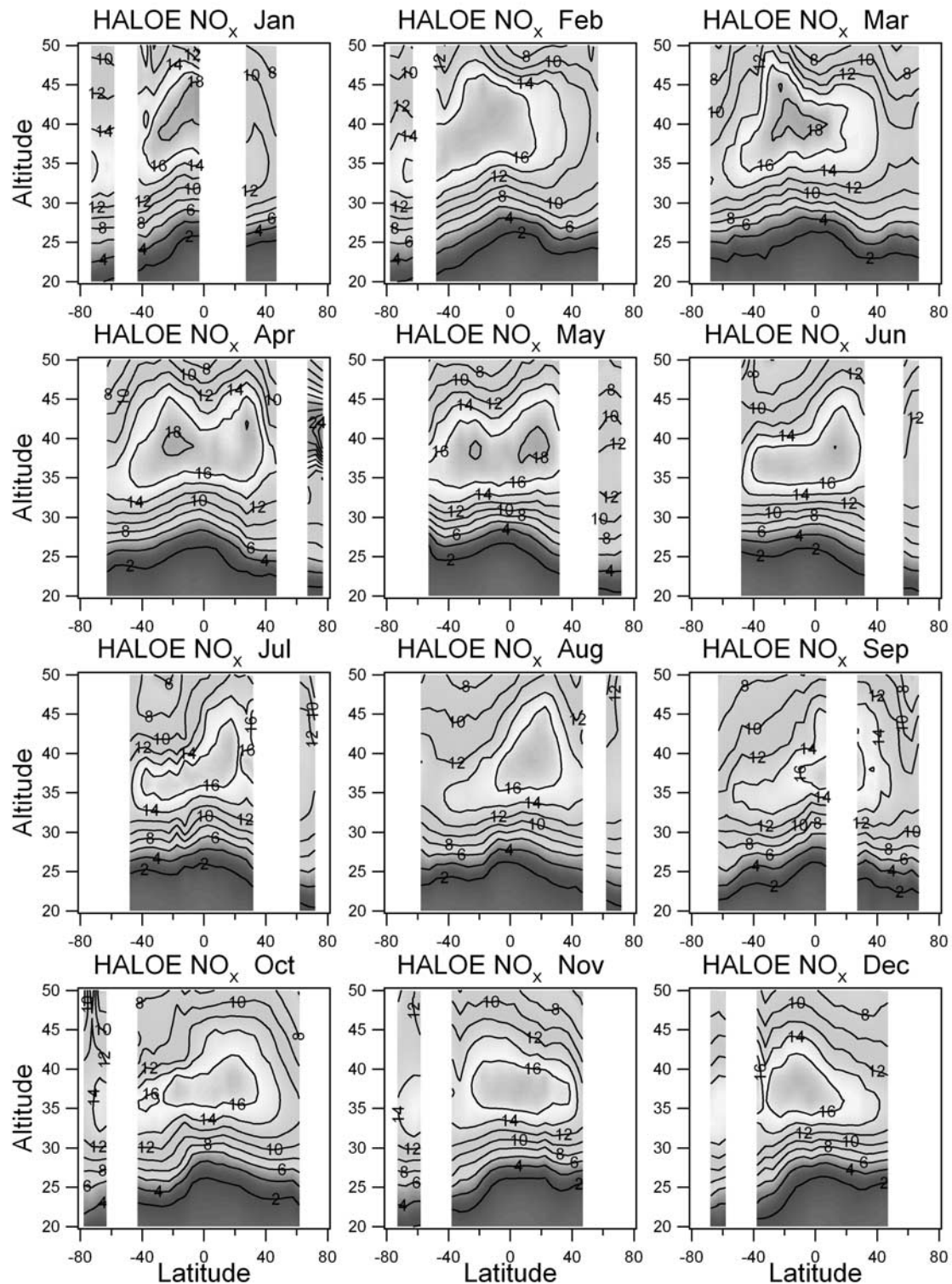


Figure 2. Latitude-altitude maps of Halogen Occultation Experiment (HALOE) NO_x (NO + NO₂) mixing ratio at sunset in ppbv for each month (average from 1999 to 2004). See color version of this figure in the HTML.

18 June is not excluded. Further studies are needed to analyze and interpret these observations in cooperation with modelers.

[16] Our understanding of the global climatology of NO and NO₂ is largely based today on solar occultation instru-

ments. It is then very interesting to compare our results with those of a well validated solar instrument. A reasonable comparison can be made with HALOE sunset NO + NO₂ data. By sunset, most of the N₂O₅ reservoir has been converted to NO and NO₂. Shortly after sunset the NO is

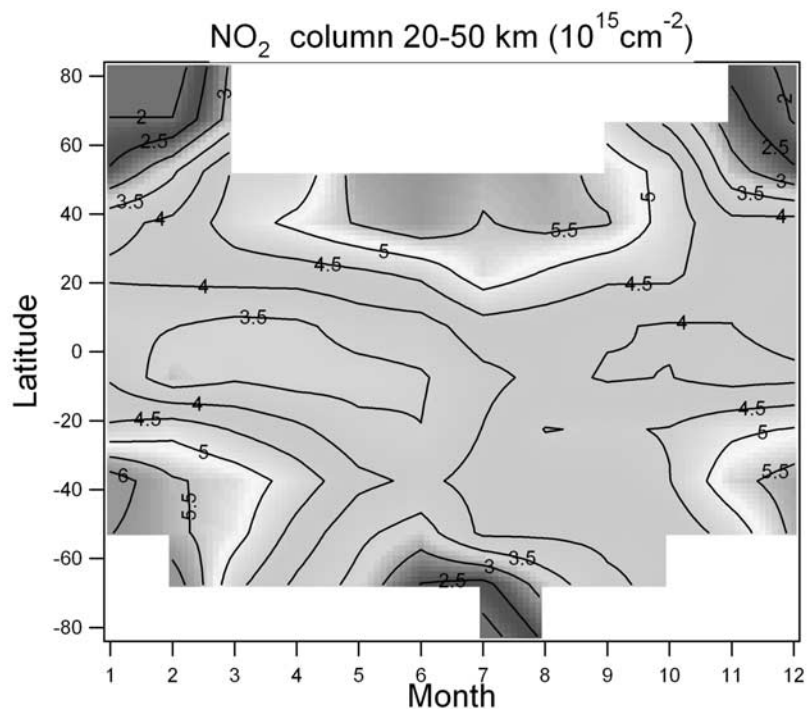


Figure 3. Time-latitude cross section of NO₂ stratospheric column (20–50 km) in 10^{15} cm^{-2} in 2003. See color version of this figure in the HTML.

converted to NO₂, which then converts slowly to N₂O₅ during the night. Thus the sum NO + NO₂ at sunset is a reasonable proxy for the NO₂ that GOMOS measures at 1000 LT. A NO_x climatology, built from HALOE sunset data from 1999 to 2004, extracted from the Web site <http://haloedata.larc.nasa.gov/home/index.php>, is presented in Figure 2. A direct comparison with HALOE data in 2003 was not possible due to too many data gaps. At low and mid latitudes, peak mixing ratios range from 16 to 18 ppmv, about 2 ppmv higher than in GOMOS NO₂. This may be explained by the slow conversion of NO₂ into N₂O₅ between sunset and 1000 LT. It is very interesting to note that the location and the shape of the maximum presents many similarities between both data sets, for instance the shift of the maximum toward the summer/autumn hemisphere and the double peak structure from March to June. At high latitude, high values observed by GOMOS are not visible in HALOE data. This may be due to the fact that they are caused by specific phenomena occurring only in 2003 like the October 2003 solar proton event or to the limited HALOE coverage at high latitudes in winter. Several space-borne instruments, as well as many ground-based UV-visible spectrometers, provide daily total columns of NO₂. For future comparison with such observations and for geophysical studies, GOMOS NO₂ stratospheric columns are computed by integration of profile concentrations between 20 and 50 km. This altitude range is chosen to integrate most of stratospheric NO₂ and to avoid too noisy data at low altitude. Contrary to mixing ratios that are maximum around 40 km, altitudes lower than 35 km contribute to 70 to 80% to the column. At midlatitude, NO₂ columns (Figure 3) follow a strong annual cycle with a maximum $> 6.0 \cdot 10^{15} \text{ cm}^{-2}$ in summer and a

minimum $< 3 \cdot 10^{15} \text{ cm}^{-2}$ in winter. Low values are observed at high latitude in winter ($< 2.0 \cdot 10^{15} \text{ cm}^{-2}$) in relation to the conversion of NO₂ into N₂O₅ in the polar night and to the heterogeneous conversion of NO_x into HNO₃ [Goutail *et al.*, 1994] in presence of polar stratospheric clouds. At low latitude, a weak annual variation is observed, in phase in the two hemispheres, with a minimum from February to April and a maximum from August to January.

4.2. NO₃

[17] The nighttime NO₃ concentration is controlled by the three reactions [Brasseur and Solomon, 1986]



Below 40 km, the thermal decomposition (reaction (3)) can be neglected and reaction (2) is fast enough for NO₃ to reach steady state equilibrium in less than 1 hour after sunset typically. NO₃ concentration is proportional to O₃ and is positively correlated with temperature through reaction (1). As pointed out by Renard *et al.* [2005], this strong dependence on temperature may induce biases in individual vertical NO₃ profiles in the presence of local temperature fluctuations. However, monthly mean profiles will not be too much affected. Above 40 km, the thermal decomposition is a significant source of NO₂ after sunset and reaction (2) is much slower. As a result, NO₃ is no more

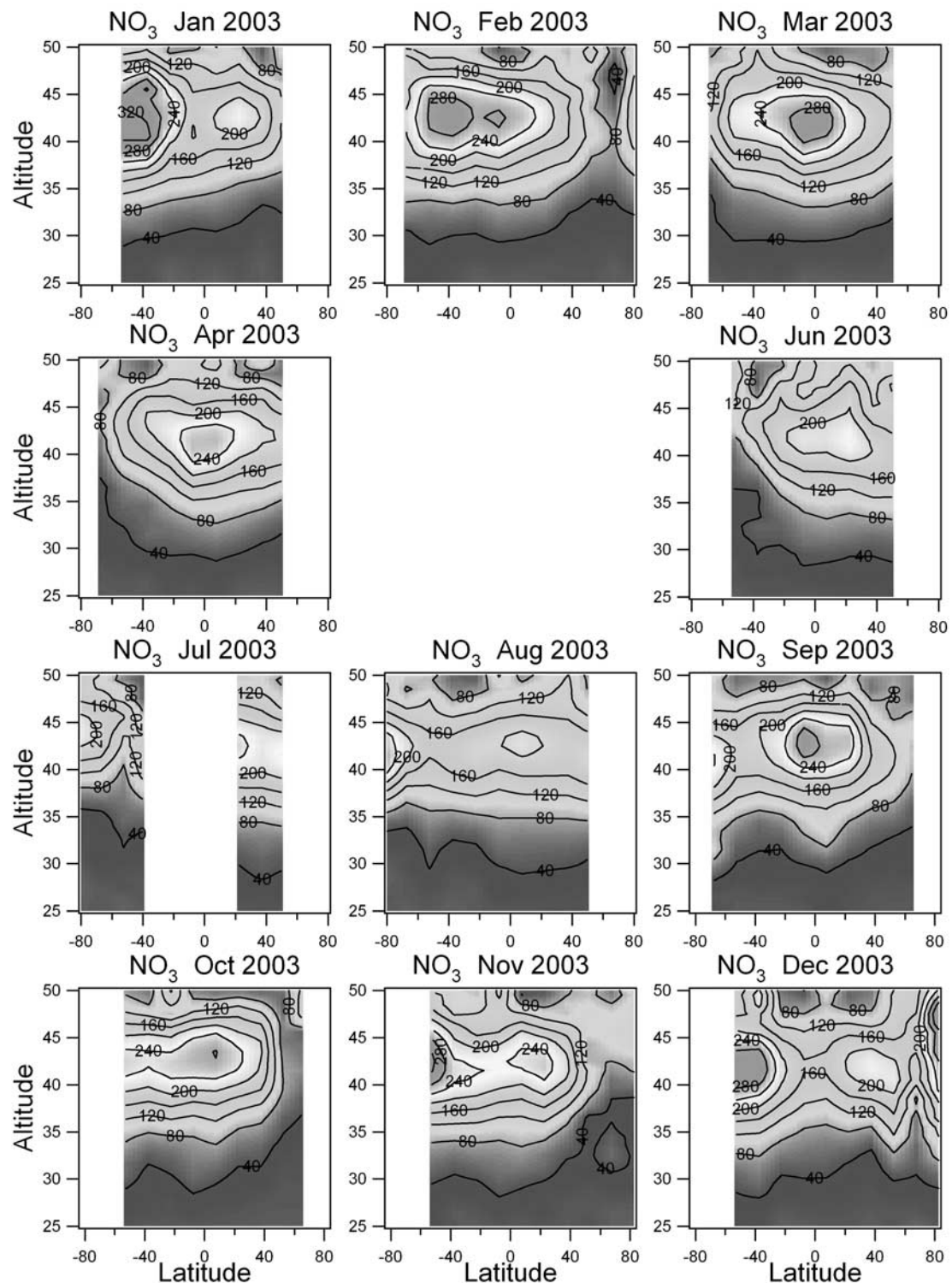


Figure 4. Latitude-altitude cross section of NO₃ mixing ratio in pptv for each month in 2003. See color version of this figure in the HTML.

at equilibrium at the time of GOMOS observations [Marchand *et al.*, 2004] and is dependent on both NO₂ and O₃ concentrations.

[18] The maximum mixing ratio is reached between 41 and 43 km (Figure 4). At mid latitude, values are higher in the summer hemisphere than in the winter one (up to

320 pptv at southern midlatitude in January). At low latitudes, the variation is more semiannual with maxima in February–March and September and minima in December–January and June–August. High values are observed at northern high latitudes in the north in December at the time of a sudden stratospheric warming.

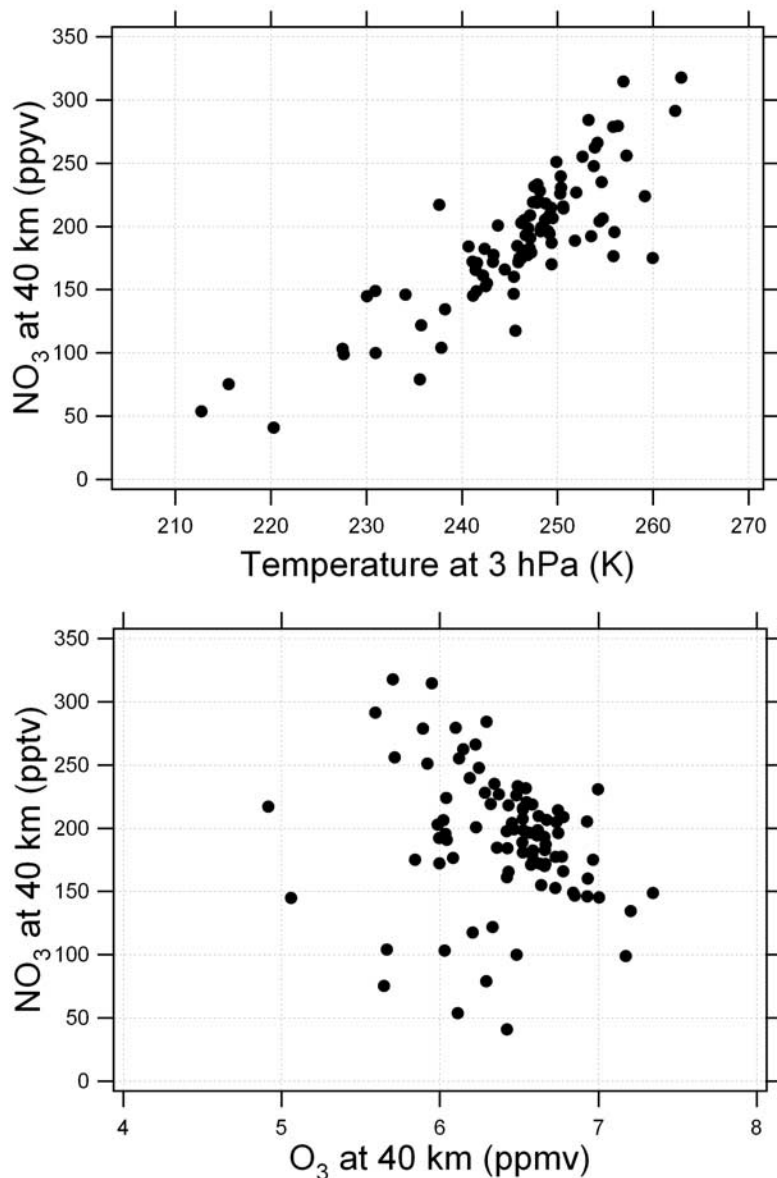


Figure 5. (top) NO₃ mixing ratio at 40 km versus European Centre for Medium-Range Weather Forecasts (ECMWF) temperature at 3 hPa (\sim 40 km). (bottom) NO₃ mixing ratio at 40 km versus O₃ mixing ratio at 40 km for all monthly averaged latitude binned data between 60°S and 60°N.

All these results suggest that NO₃ evolution is linked with upper stratospheric temperature. Warmer temperatures increase the production rate of NO₃ through the temperature dependence of reaction (1). To test this hypothesis, the monthly average of ECMWF temperature at 3 hPa (\sim 40 km) has been computed for each 15° latitude band between 60°S and 60°N and correlated with the corresponding NO₃ mixing ratio (Figure 5 (top)). There is a very clear correlation between both parameters. On the contrary, NO₃ at 40 km does not seem to be correlated with O₃ at 40 km (Figure 5 (bottom)) which is almost constant at this altitude. Another mechanism may contribute to high NO₃ values at northern high latitudes in December. Orsolini *et al.* [2005] attribute the large HNO₃ increase observed by MIPAS at this time to the

strong increase of NO_y in the Arctic upper stratosphere after the October 2003 solar proton event. This increase will enhance the production of NO₃ through reaction (1). Further studies are needed to evaluate the contribution of the two proposed mechanisms.

[19] NO₃ stratospheric columns have been computed by integration of concentration profiles in the limited altitude range 25–50 km in order to avoid too noisy data in the lower stratosphere. The seasonal evolution of the column as a function of latitude is quite similar to the evolution of the peak mixing ratio (Figure 6). A strong annual variation is observed at mid and high latitudes with a summer maximum higher in the south than in the north. In the north, the effect of the December polar stratospheric warming is also visible in the column. At low latitude, the evolution is more

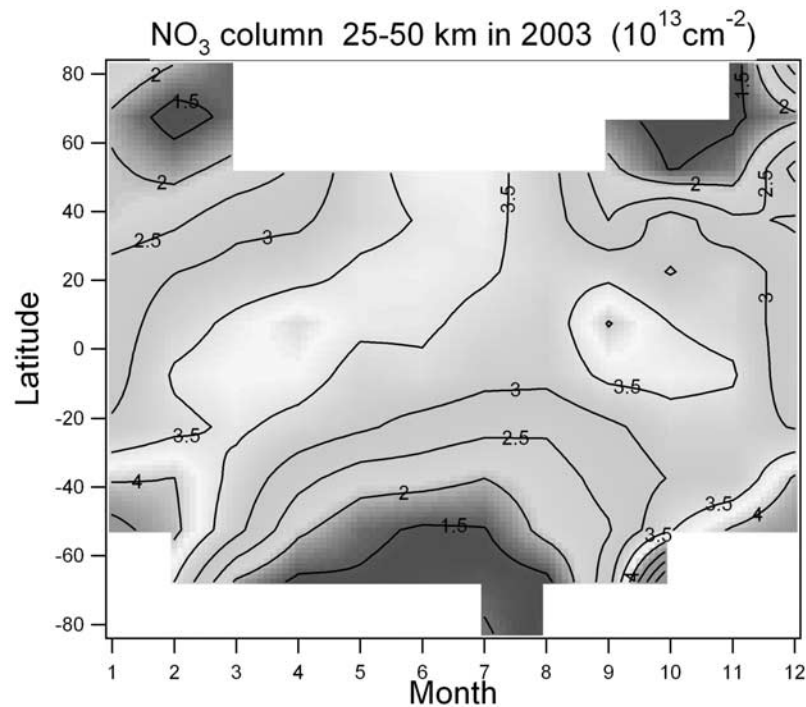


Figure 6. Time-latitude cross section of NO₃ stratospheric column (25–50 km) in 10^{13} cm^{-2} in 2003. See color version of this figure in the HTML.

semiannual with maxima in March–April and September–October and minima in December–January and June–July.

5. Conclusion

[20] GOMOS provides for the first time simultaneous global measurements of stratospheric NO₂ and NO₃ during night. The full reprocessing of 2003 data allowed us to follow the seasonal evolution of these two species as a function of latitude. The main results of this study are summarized below.

[21] 1. For NO₂, at low and mid latitudes, the mixing ratio reaches a maximum around 40 km with 14 to 16 ppbv. These values are about 2 ppbv lower than the sum NO + NO₂ measured by HALOE at sunset. The difference can be explained by the slow conversion of NO₂ into N₂O₅ between sunset and 10pm local time. The location of the maximum is shifted toward the summer/autumn hemisphere in both data sets. A high mixing ratio is also observed in upper stratosphere in November in the north polar vortex after a strong solar proton event and in July in the south vortex when air enriched in NO_x descends from the mesosphere and the thermosphere. At low latitude, NO₂ stratospheric columns follow an annual variation in phase in the two hemispheres with a minimum from February to April and a maximum from August to January. At middle and high latitudes, the annual cycle of NO₂ columns is of large amplitude with a maximum in summer.

[22] 2. For NO₃, the mixing ratio peaks at 40–45 km. At low latitude, a semiannual variation is observed in NO₃ peak concentration and stratospheric column with a maximum at equinoxes. At middle and high latitudes, the variation of NO₃ is annual with a maximum in summer.

The NO₃ mixing ratio in the upper stratosphere is strongly correlated with temperature through the thermal dependence of reaction $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$.

[23] These results are still preliminary and more validation studies will be done in the future but they provide a first full global view of two important odd nitrogen species. They are available for model studies to test photochemistry on NO_x in the stratosphere and for comparison with other satellite, in situ and ground-based observations. One of the main advantages of GOMOS is a better geographical coverage than solar occultation instruments upon which so much of our understanding today is based.

[24] **Acknowledgments.** Envisat is a European Space Agency (ESA) mission. We are especially grateful for the tremendous work of Guido Levirini and Jacques Louet for the success of the mission.

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