Constraining the $\text{N}_2\text{O}_5$ UV absorption cross-section from spectroscopic trace gas measurements in the tropical mid-stratosphere

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Abstract. The absorption cross-section of $\text{N}_2\text{O}_5$, $\sigma_{\text{N}_2\text{O}_5}(\lambda,T)$, which is known from laboratory measurements with the uncertainty of a factor of 2 (table 4-2 in JPL-2011 (Sander et al., 2011)), was investigated by balloon-borne observations of the relevant trace gases in the tropical mid-stratosphere. The method relies on the observation of the diurnal variation of NO$_2$ by limb scanning DOAS measurements (Weidner et al. (2005),Kritten et al. (2010)), supported by detailed photochemical modelling of NO$_y$ (NO$_x$=(N=NO+NO$_2$)+NO$_3$+2N$_2$O$_5$+ClONO$_2$+HO$_2$NO$_2$ +BrONO$_2$+HNO$_3$) photochemistry and a non-linear least square fitting of the model result to the NO$_2$ observations. Simulations are initialised with O$_3$ measured by direct sun observations, the NO$_y$ partitioning from MIPAS-B (Michelson Interferometer for Passive Atmospheric Sounding-Balloon) observations in similar air masses at nighttime, and all other relevant species from simulations of the SLIMCAT chemical transport model (CTM). Best agreement between the simulated and observed diurnal increase of NO$_2$ is found if the $\sigma_{\text{N}_2\text{O}_5}(\lambda,T)$ is scaled by a factor of 1.6±0.8 in the UV-C (200 - 260 nm) and by a factor of 0.9±0.26 in the UV-B/A (260 - 350 nm), compared to current recommendations. In consequence, at 30 km altitude, the $\text{N}_2\text{O}_5$ lifetime against photolysis becomes a factor of 0.77 shorter at solar zenith angle (SZA) of 30° than using the recommended $\sigma_{\text{N}_2\text{O}_5}(\lambda,T)$, and stays more or less constant at SZAs of 60°. Our scaled $\text{N}_2\text{O}_5$ photolysis frequency slightly reduces the lifetime (0.2 - 0.6%) of ozone in the tropical mid- and upper stratosphere, but not to an extent to be important for global ozone.

Keywords. Stratosphere photochemistry, limb scanning, cross-section of $\text{N}_2\text{O}_5$, UV/vis spectroscopy, photochemical modelling

1 Introduction

The NO$_x$ ozone loss cycle dominates catalytic ozone loss in the mid-stratosphere (25 - 45 km) and the ozone production via coupling with the HOx cycle below about 20 km (e.g., Brasseur and Solomon (2005)). In future it is predicted to increase further in relevance, since the emissions of its major precursor NO$_2$ are increasing, while emissions of other ozone-depleting substances (ODS) are decreasing (Ravishankara et al., 2009). Signs that this is already happening come from the recent analysis of ozone vertical profile time series from SCIAMACHY satellite instrument limb measurements (Gebhardt et al., 2013), since they show a negative trend of ozone in the tropics above 30 km and a positive trend below. The explanation most favoured by the authors is due to NO$_x$ photochemistry, which catalytically destroys stratospheric ozone (e.g., Crutzen (1970), and Johnston (1971)) (see below).

A second motivation to study the photolysis frequency of $\text{N}_2\text{O}_5$ comes through the finding of often overpredicted $\text{N}_2\text{O}_5$, most strikingly found in comparison studies of MIPAS/ENVISAT $\text{N}_2\text{O}_5$ data with predictions of a suite of photochemical transport models for the lower and middle stratosphere (ρ > 10 mbar) (e.g., Brühl et al. (2007), and Funke et al. (2011)). Unpublished SLIMCAT sensitivity runs are indicating that a more rapid photolysis of $\text{N}_2\text{O}_5$ (up to factor of 2) than supported by $\sigma_{\text{N}_2\text{O}_5}(\lambda,T)$ from JPL-2011 (Sander et al., 2011) would largely help to close this gap.

In the context of ozone loss, most crucial is how fast major nighttime NO$_y$ species (e.g., HNO$_3$, N$_2$O$_5$, and ClONO$_2$) are recycled into ozone destroying NO$_x$ at daytime. Catalytic ozone destruction by the NO$_x$ photochemistry occurs through the following reactions

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The primary source of stratospheric NO<sub>x</sub> is the photolytic destruction of N<sub>2</sub>O (R4, R5, and R6).

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R1)}
\]
\[
\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2 \quad \text{(R2)}
\]
\[
\text{net} : \text{O} + \text{O}_3 \rightarrow 2\text{O}_2 \quad \text{(R3)}
\]

(N<sub>2</sub>O is mostly emitted by biological and combustion processes at the surface, but their N<sub>2</sub>O emissions are not regulated by the Montreal Protocol (e.g., IPCC (2007), and WMO (2011)). Accordingly, atmospheric N<sub>2</sub>O concentrations are presently increasing with a rate of 0.75 ppb per year (Park et al. 2012) and WMO Press Release (No. 934)).

Four major processes determine the effect of N<sub>2</sub>O on stratospheric ozone:

1. The competition of the N<sub>2</sub>O destruction processes R4 leading to NO<sub>x</sub> production (about 7% for any N<sub>2</sub>O destroyed) and reactions R5 and R6 only destroying N<sub>2</sub>O without producing NO<sub>x</sub>.
2. The sink reactions R7 and R8

\[
\text{NO} + h\nu \rightarrow \text{N}(4\text{S}) + \text{O} \quad \text{(R7)}
\]

followed by

\[
\text{NO} + \text{N} \rightarrow \text{N}_2 + \text{O} \quad \text{(R8)}
\]

are known to destroy NO<sub>x</sub> in the middle and upper stratosphere.

3. Further it is well known that during daytime reaction R1 and the photolysis of NO<sub>2</sub>

\[
\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O} \quad \text{(R9)}
\]

readily establish a steady state between NO and NO<sub>2</sub>, thus determining the amount of NO available for the odd-oxygen destroying reaction R2.

4. The fourth major factor controlling the ozone depletion potential of NO<sub>x</sub>, and thus of N<sub>2</sub>O, are reactions leading to the so-called NO<sub<y</sub>, reservoir species (NO<sub>y</sub> = NO<sub>x</sub> + NO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub> + ClONO<sub>2</sub> + HO<sub>2</sub>NO<sub>2</sub> + BrONO<sub>2</sub> + HNO<sub>3</sub>) of which all except HNO<sub>3</sub> are important for the diurnal variation of NO<sub>x</sub>, and thus NO<sub>x</sub>-mediated ozone loss. Among them N<sub>2</sub>O<sub>5</sub> is most important in the tropical mid-stratosphere (as shown in Figure 1). First NO<sub>3</sub> has to be formed by the reaction

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 \quad \text{(R10)}
\]

then N<sub>2</sub>O<sub>5</sub> can be formed by the termolecular reaction

\[
\text{NO}_2 + \text{NO}_3 + \text{M} \rightarrow \text{N}_2\text{O}_5 + \text{M} \quad \text{(R11)}
\]

and destroyed by thermal decomposition R12, photolysis R13, and the heterogeneous reaction R14, where aerosols are abundant, i.e., in the lower stratosphere (Brasseur and Solomon, 2005).

\[
\text{N}_2\text{O}_5 + \text{M} \rightarrow \text{NO}_2 + \text{NO}_3 + \text{M} \quad \text{(R12)}
\]
\[
\text{N}_2\text{O}_5 + h\nu \rightarrow \text{NO}_2 + \text{NO}_3 \quad \text{(R13)}
\]
\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O}_{aq} \rightarrow 2\text{HNO}_3 \quad \text{(R14)}
\]

R13 is particularly relevant for the daytime increase of NO<sub>x</sub> in the tropical mid-stratosphere, since the product of photolysis rate J<sub>N<sub>2</sub>O<sub>5</sub></sub> and concentration of N<sub>2</sub>O<sub>5</sub> is the largest among the reservoir species under the given conditions (see Figure 1). The J<sub>N<sub>2</sub>O<sub>5</sub></sub> is determined by the actinic flux F(λ), the absorption cross-section of J<sub>N<sub>2</sub>O<sub>5</sub></sub>, σ<sub>N<sub>2</sub>O<sub>5</sub></sub>(λ, T) and the quantum yield for photo-dissociation φ(λ) into the channels:

\[
\text{N}_2\text{O}_5 + h\nu \rightarrow \text{NO}_2 + \text{NO}_3 \quad \text{(R15)}
\]
\[
\rightarrow \text{NO}_3 + \text{NO} + \text{O}(3\text{P}) \quad \text{(R16)}
\]
\[
\rightarrow \text{NO}_3 + \text{NO}_2* \quad \text{(R17)}
\]

(1) The four major processes determine the effect of N<sub>2</sub>O on stratospheric ozone:

\[
\text{J}_{\text{N}_2\text{O}_5} = \int F(\lambda) \cdot \sigma_{\text{N}_2\text{O}_5}(\lambda, T) \cdot \phi(\lambda) \cdot d\lambda \quad \text{(1)}
\]

The slightly temperature-dependent σ<sub>N<sub>2</sub>O<sub>5</sub></sub>(λ, T) decreases from the extreme UV-C (λ = 200 nm) to the visible spectral range (λ = 400 nm) over 8 to 9 orders of magnitude (Figure 2). On the other hand the actinic flux F(λ) strongly increases with wavelength resulting in two distinct maxima of the actinic spectrum in the mid- and upper stratosphere (i.e., in the UV-C and UV-B) (Figure 3), of which shape depends on the solar zenith angle (SZA). The short wavelength maximum of the actinic spectrum is located around λ = 220 nm and the long wavelength maximum between λ = 280 and 320 nm.

In the laboratory, σ<sub>N<sub>2</sub>O<sub>5</sub></sub>(λ, T) was first measured by Jones and Wulf (1937) and later by many others (see section 2.2). Current estimates of σ<sub>N<sub>2</sub>O<sub>5</sub></sub>(λ, T) together with its uncertainties (a factor of 2) are reported in the JPL-2011 compendium (Table 4-2). However, to our knowledge σ<sub>N<sub>2</sub>O<sub>5</sub></sub>(λ, T) has never been inferred from field observations.

Here balloon-borne measurements in the tropical mid-stratosphere of the diurnal variation of NO<sub>2</sub> (Kritten et al., 2010) are exploited to infer σ<sub>N<sub>2</sub>O<sub>5</sub></sub>(λ, T) under stratospheric conditions. For the interpretation of the measured data with respect to σ<sub>N<sub>2</sub>O<sub>5</sub></sub>(λ, T), a 1-D photochemical model is used. The model is initialised and further constrained by trace gas observations (O<sub>3</sub>, and a suite of NO<sub>x</sub> species) taken within the so-called tropical pipe over north-eastern Brazil during summer 2005. Further, an optimal estimation approach is used to minimise the quadratic difference of the measured from modelled concentration field of NO<sub>2</sub> as a function of
time and height. For this purpose $\sigma_{N_2O_5}(\lambda, T)$ is scaled by two free parameters (denoted by $s_1$ and $s_2$) in the extreme UV-C (200 - 258 nm) (denoted by $w_1$ wavelength range), and UV-B/A spectral range (260 - 420 nm) (denoted by $w_2$ wavelength range), respectively.

The paper is organised as follows. In section 2 the tools used in the study are described, including the NO$_2$ measurements, some details of the NO$_3$ photochemical modelling as well as the mathematics to retrieve $\sigma_{N_2O_5}(\lambda, T)$. Section 3 reports on the results and discusses uncertainties. Section 4 addresses the implication of our findings for stratospheric N$_2$O$_5$ and global ozone. Section 5 concludes the study.

2 Measurements, photochemical modelling, and $\sigma_{N_2O_5}(\lambda, T)$ retrieval

This section describes our approach to constrain $\sigma_{N_2O_5}(\lambda, T)$ from the NO$_2$ measurements in the tropical mid-stratosphere (Kritten et al., 2010) (section 2.1). Further the photochemical modelling including its initialisation by information gained from additional trace gas measurements in the tropical stratosphere and from simulations of the SLIMCAT CTM (section 2.2) is described. Finally the retrieval of the scaling parameters of $\sigma_{N_2O_5}(\lambda, T)$ for two wavelength intervals $w_1$ and $w_2$ (section 2.3) is discussed.

2.1 Measurements

For this study, time-dependent profiles of stratospheric NO$_2$ are used, which were measured over north-eastern Brazil (5.1$^\circ$ S, 43.6$^\circ$ W) on June 30, 2005 (see Figure 8 in Kritten et al. (2010)). During the balloon flight 187 limb spectra were recorded during 17 limb sequences, which covers 5:35 hours from local sunrise (7:30 LT) into the early afternoon (13:05 LT). The measured limb spectra were analyzed for differential slant column densities (DSCDs) using the DOAS (Differential Optical Absorption Spectroscopy) technique (e.g., Weidner et al. (2005), Kreye et al. (2013) and Platt and Stutz (2008)). Prior to the inversion of the measured DSCDs into a NO$_2$ concentration height and time field, the radiative transfer for each measurement is modelled using the radiative transfer model (RTM) McArtim (Deutschmann et al., 2011). Further, the RT calculations are validated against measured limb radiances and inferred O$_4$ and O$_3$. The measured array of NO$_2$ DSCDs is then projected into a NO$_2$ concentration versus height and time field of equal altitude ($h_i = 0.5$ km) and time spacing ($t_j = 30$ min), using the optimal estimation technique (e.g., Rodgers (2000), and Kritten et al. (2010)).

Due to decay of the NO$_3$ reservoir species during daytime, at 33 km where the NO$_2$ profile peaks, NO$_2$ increases by roughly 60% during our observation. Our analysis is limited to SZAs $\leq 85^\circ$ in order to reduce effects due to refraction which is not properly accounted for in the RTM McArtim (Deutschmann et al., 2011).

Major errors and shortcomings of our NO$_2$ measurements are the remaining pitch and azimuth angle oscillations of the balloon platform (see Figure 6 in Kritten et al. (2010)). While the former lead to a vertical jitter in the field of view, resulting in an up to $\pm 10\%$ uncertainty in the inferred NO$_2$ concentrations, the azimuth angle oscillations are more difficult to deal with. The latter is mainly due to the importance of polarisation (which is not yet considered in our RTM) of the scattered light from stratospheric limb measurements in the UV/visible wavelength range, mainly if during the course of the measurements the azimuthal scattering angle changes. Therefore, in order to remove any systematic errors due to the movement of the balloon gondola, the inferred NO$_2$ field is re-normalised using the inferred field of O$_3$. This is justified, by the constant O$_3$ concentration during the course of the measurement, and the similar optical depths at the wavelengths considered in the spectral analysis of O$_3$ and NO$_2$. For this purpose a weighting matrix is derived by dividing the retrieved O$_3$ concentration for each altitude ($h_i$) and time ($t_j$) step by the mean O$_3$ concentration of the whole balloon flight.

$$\left[NO_2,corr\right]_{i,j} = \left[NO_2,retr\right]_{i,j} \cdot \left[O_3,mean\right]_{i,j} / \left[O_3,retr\right]_{i,j}$$

It is found that the re-normalisation alters the NO$_2$ field by 15% at most. Further on in the study, the renormalised NO$_2$ field (shown in the lower panel of Figure 4) is used, rather than the field inferred in Kritten et al. (2010) (see Figure 8 therein).

2.2 Modelling of the NO$_x$ photochemical system

Since for the present study the calculation of the photolysis rates and the photochemical evolution is crucial, both deserve to be addressed. The photolysis rates are calculated by a module adopted from the SLIMCAT 3-D CTM (Bösch et al. (2003), Chipperfield (2006)) with updated molecular absorption cross-sections for N$_2$O$_5$ and HNO$_3$ (Sander et al., 2003). First, the actinic fluxes are calculated as recommended by Lary and Pyle (1991) and stored in a look-up table. Then, in order to scale the actinic fluxes to the actual atmospheric conditions, the calculated photolysis rates are interpolated to the actual pressure, temperature, SZA, and overhead ozone. For the latter an ozone profile is used, which was measured by balloon-borne solar occultation observations a few days prior to the NO$_2$ measurements (Butz et al., 2006). $J_{N_2O_5}$ skylight radiances were already validated in previous studies of our group (e.g., Bösch et al. (2003), Deutschmann et al. (2011)).

For calculation of $J_{N_2O_5}$, the $\sigma_{N_2O_5}(\lambda, T)$ based on the recommendation of the JPL-2011 compendium as shown in Figure 2) is used (Sander et al., 2011). $\sigma_{N_2O_5}(\lambda, T)$ ranges over about 9 orders of magnitude (from about $10^{-17}$ cm$^2$ at 200 nm to $10^{-26}$ cm$^2$ at 450 nm). The temperature dependence of $\sigma_{N_2O_5}(\lambda, T)$ is derived according to Harwood et al.
(1993). This only becomes significant at wavelengths greater than 280 nm, where $\sigma_{N_2O_5}(\lambda,T)$ decreases (decreasing with an increasing T-dependence for larger wavelengths).

The study of Oh et al. (1986) indicates that, besides NO$_3$, the primary photolysis products of N$_2$O$_5$ are a wavelength-dependent mixture of NO$_2$, NO$_2$ and NO + O, where NO$_2$ represents NO$_2$ in an excited electronic state (see reactions R15, R16 and R17). The measured quantum yield for the NO$_3$ production is close to unity. Since all product channels finally lead to the production of \(N\), the photolysis of two distinct wavelength regions are important for the photolysis of N$_2$O$_5$ at stratospheric conditions. It shows that two distinct wavelength regions are important for the photolysis of N$_2$O$_5$, the region \(w_1\) (200 - 258 nm) and the region \(w_2\) (260 - 420 nm). While \(\sigma_{N_2O_5}(\lambda,T)\) decreases over the whole wavelength region, the actinic flux modulates the actinic spectrum, mainly due to the absorption by O$_3$ and O$_2$. The minimum between the two maxima is caused by the combined effects of the O$_3$ absorption in the Hartley band, and the O$_2$ absorption in the Herzberg band. Thus, overall O$_2$ and O$_3$ are crucial for the photolysis of N$_2$O$_5$ in the UV-C. The relative importance of each maximum depends on altitude and SZA. Therefore, if overhead ozone and total air mass is held fixed, observations at different altitudes and SZAs may provide independent information on the contribution of each wavelength region to J$_{N_2O_5}$. Noteworthy is also that in the wavelength range \(w_1\), \(\sigma_{N_2O_5}(\lambda,T)\) is temperature-independent and in \(w_2\) temperature-dependent (Figure 2).

The temporal evolution of the NO$_x$ species is modelled on 11 height levels (located between 665 K potential temperature (25.5 km) and 1099 K (35.5 km)) using the 1-D chemistry model LABMOS, which is an updated version of the model used by Bösch et al. (2003). It includes all relevant photochemical reactions of oxygen, nitrogen, hydrogen, chlorine, and bromine species according to kinematic and thermochemical data compiled in Sander et al. (2011). The model was integrated for 10 days using the commercial Fac-simile software . All modelled data shown are taken from the 10th day of the respective model run, in order to allow for spin-up of the NO$_x$ partitioning.

The model is initialised for most species using the output of SLIMCAT simulations (Chipperfield, 2006) (run-id 336) for 5° N, 43° E for 2:00 LT on 17 June, 2005, except for NO$_x$ species and O$_3$. For initialisation of the NO$_x$ species HNO$_3$, N$_2$O$_5$, ClONO$_2$, HO$_2$NO$_2$, and BrONO$_2$, the measurements of the MIPAS-B (Michelson Interferometer for Passive Atmospheric Sounding-Balloon) instrument are taken, which were recorded 17 days prior to the mini-DOAS NO$_2$ measurements (e.g., Wetzel et al. (2002) and unpublished data). The model is further constrained by ozone measured by solar occultation measurements taken from the LIMA/DOAS payload (Limb Profile Monitor of the Atmosphere/Differential Optical Absorption Spectroscopy) 13 days prior to the NO$_2$ measurements.

Small mismatches in measured and modelled total NO$_y$ are again removed by re-normalisation with the factor (nf) of the concentrations (NO$_y$) of the different NO$_y$ species (Wiegela et al., 2009):

$$nf = NO_y,MIPAS-B/NO_y,SLIMCAT,$$

(3)

such that the NO$_y$ partitioning given by SLIMCAT is preserved, but the total amount is constrained to the NO$_x$ measured by the MIPAS-B instrument. Depending on the altitude, the normalisation factor ranges between 1 and 1.2. Figure 1 provides an overview on how the different NO$_x$ species contribute to daytime NO$_x$ production at different altitudes. Here the lower boundary of the striped area denotes the temporal evolution of the particular gas, and the striped area shows the total amount of NO$_x$, which is released by photolysis from the considered NO$_x$ species. The dominant role of N$_2$O$_5$ destruction (red) for NO$_x$ formation by R11, and R12 in the tropical mid-stratosphere at daytime is evident. In contrast all the other NO$_x$ species including HNO$_3$ contribute to less than 10% to the NO$_x$ increase during daytime.

2.3 Retrieval of $\sigma_{N_2O_5}(\lambda,T)$

If the model was complete (i.e., there was no missing chemistry), a comparison of measurements and model should provide information about the accuracy of the model and its components. We refer to the model output as NO$_{2calc}$, and the measured NO$_2$ as NO$_{2meas}$. However, ‘calculated’ concentrations are not totally independent from the measurements, since O$_3$ is relevant for the calculation of the actinic fluxes (see Section 2.2) and the partitioning of NO$_y$ contributes to NO$_2calc$. Figure 4 shows NO$_{2calc}$ and NO$_{2meas}$ in the upper and lower panel, respectively. In the following we describe how the parameters $s_1$ and $s_2$ are retrieved from the measured and modelled field of NO$_2$. They are defined by

$$s_1 \cdot \sigma_{N_2O_5}(200 - 258\,\text{nm})_{lab} = \sigma_{N_2O_5}(200 - 258\,\text{nm})_{ret},$$

(4)

$$s_2 \cdot \sigma_{N_2O_5}(260 - 350\,\text{nm})_{lab} = \sigma_{N_2O_5}(260 - 350\,\text{nm})_{ret},$$

(5)

where the subscripts lab and ret and denote the laboratory measured and retrieved $\sigma_{N_2O_5}$, respectively. The measurement vector $y_i$ is given by the subsequently measured NO$_2$ concentrations for $i$ and $t_j$ (Section 2.1)

$$y_{i,j} = NO_2(h_i,t_j)$$

(6)

and the state $x$ is defined by the scaling factors $s_1$ and $s_2$.

$$x_k = s_k$$

(7)
The sensitivity of the NO$_2$ field to $s_1$ and $s_2$ can be quantitatively expressed by a weighting function or Jacobian matrix of derivatives of [NO$_2$]$_{i,j}$ with respect to the parameters $s_1$ and $s_2$, i.e., $\partial [\text{NO}_2]_{i,j}/\partial s_k$. For a given NO$_2$ profile with the indices $i$ for a given altitude $h_i$ and $j$ for a given time $t_j$ (Figure 5), the Jacobian with respect to $s_1$ and $s_2$ reads

$$K_{i,j,k} = \frac{\partial y_{i,j}}{\partial x_k},$$

(8)

The forward model $F(x) = y$ is constructed from the photo-chemical model as described in Section 2.2. The inferred sensitivity (i.e., Jacobians $K_{i,j,k}$) for $s_1$ and $s_2$ is shown in Figure 5. For $s_1$, it is a factor of 6 lower than for $s_2$, but both peak around 28 to 35 km altitude, i.e., where the measurements are taken. The maximum sensitivity ($\partial [\text{NO}_2]_{i,j}/\partial s_k$) is more extended in time for $s_2$ than for $s_1$, since in the UV-C ($w_1$) the spectral actinic flux is more dependent on SZA as compared to the UV-B/A wavelength range ($w_2$). Furthermore $\partial [\text{NO}_2]_{i,j}/\partial s_1$ peaks at higher altitudes as compared to $\partial [\text{NO}_2]_{i,j}/\partial s_2$, since attenuation in the UV-C occurs at smaller overhead air masses as compared to the UV-B/A wavelength range. For the purpose of a retrieval of $s_1$ and $s_2$ the matrix with elements $y_{i,j}$ is transformed into a 1-dimensional vector $y_i$ that contains the NO$_2$ profiles for subsequent time steps $t_j$. Similarly, the kernel $K_{i,j,k}$ is transformed into a 2-dimensional matrix $K$. In order to provide enough information on the state and to make the inversion mathematically feasible we need an additional constraint. Since an a priori $x_a$ and a priori covariance (it’s error matrix) is available and well defined through the JPL recommendations, we chose the optimal estimation technique (Rodgers, 2000) to estimate $s_1$ and $s_2$. Here, the retrieved state $\hat{x}$ is constructed from both, prior information and the measurements, each weighted by the covariances $S_a$ and $S_s$, respectively. Adopting the JPL recommendations as priori constraints, the a priori scaling factors $s_1$ are unity and the associated a priori covariance matrix is diagonal with values of 2 in the diagonal.

The relationship between measurement and state is examined by the cost function defined by

$$\chi^2 = \left(\hat{x} - x_a\right)S^{-1}_a(\hat{x} - x_a)^T + (y_{\text{mod}} - y_{\text{meas}})S^{-1}_e(y_{\text{mod}} - y_{\text{meas}})^T$$

(9)

Since the measurement and the state do not linearly map, the state $x$ is iteratively retrieved from (the subscript $n$ now denotes the $n$th step)

$$\hat{x}_{n+1} = x_n + (S_n^{-1} + K_n^T S^{-1}_e K_n)^{-1}$$

$$[K_n^T S^{-1}_e (y - F(x_n)) - S_n^{-1}(x_n - x_a)]$$

(10)

where $K_n$ is derived before each iteration for the current state $x_n$. As the starting state we choose $x_0 = x_a$. The diagonal elements of the measurement covariance $S_e$ represent the squared error of the retrieved NO$_2$ measurements. For convergence criteria a certain step size from iteration $n$ to $n+1$ is defined (Rodgers, 2000)

$$\sqrt{(x_{n+1} - x_n)^2} \leq 0.04,$$

(11)

which is about one order of magnitude smaller than the expected noise error of the solution, as derived in Section 3.1.

3 Results and Discussion

Figure 6 shows $\chi^2$ in the parameter space $s_1$ and $s_2$, where the minimum region ($\chi^2 = 30$) is located at around $s_1 = 1.2$ to 2.6 and $s_2 = 0.7$ to 1.1. After 10 iterations the global minimum is found at $s_1 = 1.6$ and $s_2 = 0.9$, i.e. our retrieval indicates a $\sigma_{N_2O_5}(\lambda, T)$ a factor 1.6 larger in the UV-C spectral range and a factor 0.9 smaller in the UV-B/A spectral range as compared to the recommended value in JPL-2011, with retrieval uncertainties of ±0.80 and ±0.26 for $s_1$ and $s_2$, respectively (see next section). Figure 6 shows the inferred result in the $s_2/s_1$ space together with their uncertainties, and the recommended JPL-2011 values. Figure 7 shows the resulting $\sigma_{N_2O_5}$. Figure 4 shows the modelled (unscaled $s_1$ and $s_2$ in the upper panel, scaled $s_1$ and $s_2$ in the middle panel) and the measured diurnal NO$_2$ concentration (lower panel). Since there is still some discrepancy in the diurnal behaviour of the forward modelled state and the measurement, in the next section we investigate to what extent the errors and uncertainties of the measurement, as well as errors and uncertainties of the forward model, propagate into the inferred $s_1$ and $s_2$ values (see Table 1 for an overview on the errors and uncertainties).

3.1 Retrieval uncertainties

The measurement error ($S_{\text{noise}}$) of NO$_2$ has already been discussed by Kritten et al. (2010). According to Rodgers (2000), the propagation of the measurement noise into the retrieval noise can be quantified by

$$S_{\text{noise}} = (K^T S^{-1}_e K)^{-1}.$$  

(12)

which leads to $1-$σ errors of ±0.80 and ±0.26 for $s_1$ and $s_2$, respectively.

3.2 Uncertainties in the forward model

We now discuss errors and uncertainties of $s_1$ and $s_2$ due to uncertainties in the forward model parameters, which are input parameters that influence the state but are not retrieved (Rodgers, 2000). Since the model is not linear in the forward model parameters, additional local retrievals of $s_1$ and $s_2$ at both the lower and upper boundary of the uncertainty range of these parameters are required. The difference in the retrieved $s_1$ and $s_2$ compared to the undisturbed case is taken as a measure for the uncertainty. The uncertainties are
not symmetrical, hence in each case an upper and a lower range of uncertainty is given. The forward model parameters in this study are input parameters to the chemical model. Among the many input parameters (i.e. model initialisation parameters as well as kinetic and thermochemical data), only those parameters which arguably exert the most influence on the results are considered. For model initialisation, these are total NO$_x$ and O$_3$, and the absorption cross-section of NO$_2$. We also discuss the uncertainty in the actinic flux going into the calculation of $J_{N_2O_5}$. The following results are obtained:

1. Initialisation of NO$_2$Y: As outlined above (section 2.2), the total amount of NO$_x$ is initialised from MIPAS-B measurements. The accuracy of the MIPAS-B NO$_x$ measurements above 20 km ranges between 4 and 7%. When initialising the model with NO$_x$ at the lower boundary of the uncertainty range, the retrieval gives $s_1 = 2.1$ and $s_2 = 1.0$. When initialising the model with NO$_x$ at the upper boundary of the uncertainty range, the retrieval gives $s_1 = 1.3$ and $s_2 = 0.7$. Accordingly the uncertainties due to initialisation of NO$_x$ are $\Delta s_1 = +0.5/-0.3$ and $\Delta s_2 = +0.1/-0.2$.

2. Initialisation of O$_3$: As outlined above (section 2.2), the O$_3$ profile is initialised from direct sun DOAS observations. The accuracy of these measurements above 20 km ranges between 5 and 29%. When initialising the model with O$_3$ at the lower boundary of the uncertainty range, the retrieval gives $s_1 = 1.3$ and $s_2 = 0.7$. When initialising the model with O$_3$ at the upper boundary of the uncertainty range, the retrieval gives $s_1 = 1.9$ and $s_2 = 1.2$. Accordingly, the uncertainties due to initialisation of O$_3$ are $\Delta s_1 = +0.3/0.4$ and $\Delta s_2 = +0.3/-0.2$.

3. Absorption cross-section of NO$_2$ (see reaction R9): The combined uncertainty of the NO$_2$ absorption cross-section and the quantum yield is a factor of 1.2 (Sander et al., 2011). When calculating the photolysis rates of NO$_2$ at the lower boundary of the uncertainty range of $\sigma_{NO_2}(\lambda,T)$, the retrieval gives $s_1 = 1.1$ and $s_2 = 0.6$. When calculating the photolysis rates of NO$_2$ at the upper boundary of the uncertainty range of $\sigma_{NO_2}(\lambda,T)$, the retrieval gives $s_1 = 2.2$ and $s_2 = 1.2$. Accordingly the uncertainties due to $\sigma_{NO_2}(\lambda,T)$ are $\Delta s_1 = +0.6/-0.6$ and $\Delta s_2 = +0.3/-0.3$. Evidently, despite its relatively small uncertainty, uncertainties in $\sigma_{NO_2}(\lambda,T)$ directly propagate into the modelled NO$_2$ concentration.

4. The rate constant $k_{NO+O_3}$ (see reaction R1): The uncertainty of the rate constant $k_{NO+O_3}$ is temperature-dependent (Sander et al., 2011) and varies at temperatures relevant for this study between a factor of 1.30 and 1.42. When implementing a rate constant $k_{NO+O_3}$ at the lower boundary of the uncertainty range, the retrieval gives $s_1 = 2.1$ and $s_2 = 1.5$. When implementing a rate constant $k_{NO+O_3}$ at the upper boundary of the uncertainty range, the retrieval gives $s_1 = 0.7$ and $s_2 = 0.6$. Accordingly, the uncertainties due to the rate constant $k_{NO+O_3}$ are $\Delta s_1 = +0.5/-0.9$ and $\Delta s_2 = +0.6/-0.3$.

5. Actinic flux and $J_{N_2O_5}$: Another uncertainty in the calculated photolysis rates is due to uncertainties of the calculated actinic flux. In the mid- and upper stratosphere, uncertainties of the actinic flux are primarily due to the contribution of the direct solar irradiance rather than the contribution of scattered radiation from above or even from below (due to the absorption of ozone below 315 nm) for the altitude of interest (e.g., Madronich et al. (1985), Madronich (1987) and Bösch et al. (2003)). Scattering from below by clouds is not considered, because we could find no evidence of coulds through a comparison of modelled and measured limb radiances. Therefore, we assume major uncertainties in the spectral actinic flux relevant for $J_{N_2O_5}$ are primarily due to (a) the solar activity-dependent irradiance being particularly variable in the UV-C and UV-B spectral ranges, (b) overhead ozone, and (c) overhead O$_2$.

(a) In the UV-C and UV-A/B spectral ranges the spectral irradiance is known to be largely correlated with the solar activity (Foukal et al., 2006). Our measurements were conducted during the declining phase of solar cycle 23 in June 2005 with total solar sunspot numbers being around 30 (i.e. about 25% of the maximum sunspot number of cycle 23 seen in 2001). Therefore, it is rather likely that the solar radiation in the UV-C and UV-A was not particularly elevated during our measurement (Foukal et al., 2006). Further, during balloon flights conducted in 1996 and 1997, we measured the actinic flux relevant for photolysis of NO$_2$ in a similar descending phase solar cycle 22. No significant departure of the measured and modelled actinic fluxes was found (Bösch et al., 2003). Also, during three balloon flights conducted in 2003 and 2004, we measured the spectral solar irradiance. For the 325 - 370 nm spectral range reasonable agreement was found between our irradiance and the measurements of SIM, SCIAMACHY, SOLSPEC and Modtran 3.7 (within < 5%), indicating no abnormal increase in the spectral irradiance in the UV-A in 2003 and 2004 when the sunspot numbers were larger than in 2005 (Gurli et al., 2005). In addition, recent solar irradiance measurements claim that from solar maximum to minimum, solar radiation in the extreme UV may decrease four to six times more than predicted by models (Haigh et al., 2010). Accordingly, we see no reason to assume that radiation in the UV-C was particularly elevated during our measurements, at least not in an amount to explain an increased $s_1$ value.

(b) Ozone in the mid- and upper stratosphere used to scale the actinic flux was measured on several occasions during the same campaign. For our simulation overhead ozone measured at high accuracy by solar occultation spectroscopy is used (e.g., Butz et al. (2006) and Dorf et al. (2008)).

(c) Further the total overhead airmass and thus O$_2$ is determined by in-situ measured pressures and temperatures, and any significant departure would have been detected through a curved rather than straight line in a Langley plot of measured slant column amount of ozone (or BrO) versus total air mass (e.g., see Figure 2 in Dorf et al. (2008)).

Finally, the impact of a potentially too coarse wavelength grid (1 nm) in calculation of $J_{N_2O_5}$ (equation 1) should be
very small because of the lack of differential structures in $\sigma_{N_2O_5}(\lambda, T)$ (Trentmann et al., 2003). In conclusion, the error in the calculated $J_{N_2O_5}$ due to uncertainties of the calculated actinic flux is assumed to be negligible.

The individual uncertainties and errors of our study on $\sigma_{N_2O_5}(\lambda, T)$ are summarised in Table 1. In order to estimate a total error, we added positive and negative deviations separately in quadrature, even though we are aware that a Monte Carlo estimation would be more adequate, we used this approximation due to high computational costs of a Monte Carlo approach. The individual noise and forward model parameter errors add to a total error of $+1.26$ to $-1.44$ for $s_1$ and $+0.79$ to $-0.57$ for $s_2$.

4 Implications

Now we relate our results concerning $\sigma_{N_2O_5}(\lambda, T)$ to earlier discrepancies of measured and modelled $N_2O_5$ in the stratosphere and assess possible implications on global ozone. Previous inter-comparisons of measured and modelled $N_2O_5$ in the stratosphere reveal the following:

(a) The studies of Brühl et al. (2007) and Funke et al. (2011) also addressed inter-comparisons of $N_2O_5$ measured by ENVISAT/MIPAS. In particular for the retrieval from the IMK/IAA (Institut für Meteorologie und Klimaforschung and Instituto de Astrofísica de Andalucía) Brühl et al. (2007), stated a problem to reproduce the observed nighttime partitioning between $N_2O_5$ and NO$_2$ in the middle stratosphere using the recommended set of reaction coefficients and photolysis data, while for the Halloween solar proton event in late October 2003, the inter-comparison of measurements and model resulted in much larger modeled than measured $N_2O_5$, except for the KASIMA model (Funke et al., 2011).

(b) At the same time, Wolff et al. (2008) stated a low bias ($-0.25$ ppb) of ACE-FTS $N_2O_5$ relative to the MIPAS IMK-IAA retrieval for the middle stratosphere around 30 km.

(c) Moreover, in a recent study, Wetzel et al. (2012) found slightly larger measured MIPAS-B $N_2O_5$ concentrations than those modelled by EMAC (ECHAM/MESSy Atmospheric Chemistry) (e.g., Jöckel et al. (2005)) for the mid-stratosphere (22 - 34 km) at high latitudes during mid winter, i.e. SZA > 86°.

More recent sensitivity studies using SLIMCAT (not shown) indicate that in order to reconcile modelled and measured $N_2O_5$ for the studies mentioned in (a), the $N_2O_5$ photolysis frequency need to be increased by at least a factor 1.5 to 2 in the UV-B/A. However an increase in UV-B/A photolysis of $N_2O_5$ by a factor 1.5 to 2 would deteriorate the existing agreement between $N_2O_5$ concentrations measured by ACE-FTS and simulated by SLIMCAT for sunrise and sunset (finding b), but at the same time it would potentially increase the discrepancy found in the study of Wetzel et al. (2012). Finally, such an increase is not supported by the result of our study.

A possible increase of $\sigma_{N_2O_5}(\lambda, T)$ in the UV-C spectral range as indicated by the present study would not resolve the discrepancies found in (a), mainly since below 10 mbar the UV-C radiation rapidly contributes less and less to the $N_2O_5$ photolysis as the altitude becomes lower. At the same time, it may not modify finding (b), and at best it would only slightly improve the mismatch found in (c).

Therefore, it is rather likely that the mismatch of the ENVISAT/MIPAS $N_2O_5$ with the various model predictions is not due to an incorrect $\sigma_{N_2O_5}(\lambda, T)$ used in the models, but due to any other reason.

In order to assess the consequences of our finding on global ozone, sensitivity simulations for the modified $\sigma_{N_2O_5}(\lambda, T)$ were performed using the SLIMCAT 3-D CTM (e.g., Chipperfield (1999), and Chipperfield (2006)). The model was run at a horizontal resolution of $5.6^\circ \times 5.6^\circ$ with 32 levels between the surface and ~60 km. The model was forced using European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim data and used the model’s standard stratospheric chemistry scheme. A first run (run R) used JPL-2011 photochemical data. A second run (N) was identical to run R but used the scaled values for $\sigma_{N_2O_5}$ derived in this work. Run N was initialised from run R in July 2007 and integrated for 2 years. Output from 2008 was used for this exercise.

Figure 8 shows the percentage change in annual mean O$_3$, NO$_2$ and $N_2O_5$ between runs N and R for 2008, along with the O$_3$ change in September. $N_2O_5$ decreases above 30 km by up to 4% in the annual (24-hour) mean due to the increased photolysis at short wavelengths. Below 30 km (35 km near the poles) NO$_2$ increases by up to 5% due to the slower photolysis at longer wavelengths. The change in NO$_2$ shows an opposite pattern reflecting the changing partitioning between NO$_x$ and $N_2O_5$. Overall, the impact of the change in $\sigma_{N_2O_5}$ on ozone is small. In the mid-stratosphere (30-35 km) the increased NO$_x$, which is the main sink of odd oxygen in this region, leads to an O$_3$ decrease of about 0.25% with the scaled $\sigma_{N_2O_5}$. Below 30 km the ozone response changes sign, consistent with the NO$_x$ change, but it is still only around 0.25%. In September O$_3$ loss inside the polar vortex is suppressed slightly (-0.6% change).

5 Summary and Conclusion

For the first time the absorption cross-section of $N_2O_5$, $\sigma_{N_2O_5}(\lambda, T)$ is constrained from measurements of the diurnal increase in NO$_2$ in the tropical mid-stratosphere. It is found that in the UV-C (200 - 260 nm) $\sigma_{N_2O_5}(\lambda, T)$ may be larger by a factor of 1.6 ± 0.8, and in the UVB/A (260 - 350 nm) smaller by a factor of 0.9 ± 0.26 as compared to the JPL-2011 recommendations. Additional uncertainties of our study are due to uncertainties of the forward model parameters, which are estimated to be up to +0.6 to -0.9 in the UV-C and up to +0.6 to -0.3 in the UV-B/A. A total error is esti-
imated to be +1.26 to -1.44 in the UV-C and +0.79 to -0.57 in the UV-B/A. The outcome of our study could be improved if other NO₅ species (e.g., by MIPAS-B) were simultaneously measured. This was unfortunately not possible in a second attempt to simultaneously operate the MIPAS-B and miniDOAS instrument in a joint deployment over North-Eastern Brazil 2008 due to technical constraints.

Overall, above 30 km N₂O₅ concentrations decrease by to 4% in the annual (24-hour) mean due to the increased photolysis at short wavelengths, when using the retrieved \( \sigma_{N₂O₅}(\lambda, T) \). Below 30 km (35 km near the poles) N₂O₅ increases by up to 5% due to the slower photolysis at longer wavelengths. For this altitude region in some cases lower measured than modelled N₂O₅ have been reported for the late morning lower stratosphere (e.g., in yet unpublished comparison studies of SLIMCAT simulations with EMVISAT-MIPAS N₂O₅ measurements), which could be reconciled increasing \( \sigma_{N₂O₅}(\lambda, T) \) in the UV-B/A wavelength range by up to a factor of 2 compared to the JPL-2011 recommendations (e.g., as indicated by recent SLIMCAT runs). Increasing the N₂O₅ photolysis in the UV-C according to our finding is not enough to eliminate the stated mismatch of measured and modelled N₂O₅ for altitudes above 30 km.

Therefore firm conclusions on a larger UV-C N₂O₅ absorption cross section as indicated by our study can not be drawn from previous measurement versus model inter-comparison studies.

Further a sensitivity test using our revised versus the JPL-2011 recommended \( \sigma_{N₂O₅}(\lambda, T) \) show little effects on global ozone. Above 30 km, where UV-C light is strongly contributing to the N₂O₅ photolysis, the increase in \( \sigma_{N₂O₅}(\lambda, T) \) (1.6 ± 0.8 in the \( w₁ \) wavelength region), leads to an increase in NO₂ and through R2 to 0.2% less ozone at most. Below 30 km, where N₂O₅ photolysis due to UVB/A light is more important, our smaller \( \sigma_{N₂O₅}(\lambda, T) \) (0.9 ± 0.26 in the \( w₂ \) wavelength region) leads to slightly more ozone, i.e. 0.2% in the mid-latitude stratosphere, and as much as 0.6% in the 20 - 25 km region over the Antarctic in spring.

Finally our approach could also be used to retrieve more and other parameters from simultaneous atmospheric measurements of the relevant NO₅ species, including a tighter assessment of the absorption cross-section of NO₂.

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Table 1. Uncertainties in the retrieval of $s_1$ and $s_2$.

<table>
<thead>
<tr>
<th>Retrieved Value</th>
<th>Noise</th>
<th>NO$_y$ Initialisation</th>
<th>O$_3$ Initialisation</th>
<th>$\sigma_{NO_y}$</th>
<th>$k_{NO_y+O_3}$ total</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s_1$</td>
<td>1.6</td>
<td>$\pm0.80$</td>
<td>+0.5,-0.3</td>
<td>+0.3,-0.6</td>
<td>+1.26,-1.44</td>
</tr>
<tr>
<td>$s_2$</td>
<td>0.9</td>
<td>$\pm0.26$</td>
<td>+0.1,-0.2</td>
<td>+0.3,-0.3</td>
<td>+0.79,-0.57</td>
</tr>
</tbody>
</table>

Fig. 1. Temporal evolution of N$_2$O$_5$ (red), HNO$_3$ (green) and the sum of other NO$_x$ species (ClONO$_2$ + HO$_2$NO$_2$ + BrONO$_2$, blue) for different altitudes of the tropical mid-stratosphere (5.1° S, 43.6° W). The lower boundary of the striped area denotes the temporal evolution of the particular gas, and the striped area shows the total amount of NO$_x$, which is released by photolysis from the considered NO$_y$ species. Note that the release from N$_2$O$_5$ is double due to two N atoms.

Fig. 2. Absorption cross-section and uncertainty of $\sigma_{N_2O_5}(\lambda,T)$ as recommended by JPL 2011 (Sander et al., 2011) (yellow area). For this study, $\sigma_{N_2O_5}(\lambda,T)$ is divided into two wavelength regions $w_1$ and $w_2$. No temperature dependence of $\sigma_{N_2O_5}(\lambda,T)$ is reported for $w_1$, the T dependence for $w_2$ is indicated by different colours.
Fig. 3. Actinic spectrum of $N_2O_5$ (i.e., the product of $\sigma_{N_2O_5}(\lambda,T)$ (at 230 K) and modelled actinic fluxes) for an overhead ozone column of 283 Dobson Units, and different SZAs at 30.5 km.
Fig. 4. Temporal evolution of the NO$_2$ concentration in the tropical mid-stratosphere (5.1° S, 43.6° W) for June 13, 2005, using the JPL-2011 recommendation for $\sigma_{N_2O_5}(\lambda, T)$ i.e., $s_1 = 1.0$ and $s_2 = 1.0$ (upper panel). Middle panel: Same as in the upper panel, but with the inferred $s_1 = 1.6$ and $s_2 = 0.9$ (middle panel). Lower panel: Measured NO$_2$. Units are given in molec/cm$^3$. 
Fig. 5. Sensitivity of the NO₂ concentration in our model to the scaling factors $s_1$ (left panel) and $s_2$ (right panel) on the absorption cross-section of N₂O₅. Units are given in $10^7$ molec/cm³. The altitude region used for the analysis is marked by black lines.

Fig. 6. $\chi^2$ as a function of $s_1$ and $s_2$, as given in Eq. (9). The inferred global minimum is shown in red together with the total error due to noise error of the retrieval. The corresponding JPL-2011 values are given in black.
Fig. 7. $\sigma_{N_2O_5}(\lambda, T)$ measured in the laboratory (JPL-2011, shown in light blue) and inferred in the present study (shown in pink).
Fig. 8. Difference in zonal mean fields (%) for 2008 from the run of the SLIMCAT 3-D CTM with scaled $J_{N_2O_5}$ (run N) minus the run with recommended JPL-2011 kinetics (run R) for (a) annual mean $O_3$, (b) September mean $O_3$, (c) annual mean $NO_2$, and (d) annual mean $N_2O_5$. Note irregular contour interval.