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Measurement from sun-synchronous orbit of a reaction rate controlling the diurnal NO_x cycle in the stratosphere

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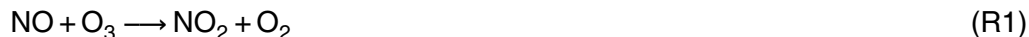


Abstract

A reaction rate associated with the nighttime formation of an important diurnally varying species, N_2O_5 , is determined from MIPAS-ENVISAT. During the day, photolysis of N_2O_5 in the stratosphere contributes to nitrogen-catalysed ozone destruction. However, at night concentrations of N_2O_5 increase, temporarily sequestering reactive NO_x ($\text{NO} + \text{NO}_2$), in a natural cycle which regulates the majority of stratospheric ozone. In this paper, the reaction rate controlling the formation of N_2O_5 is determined for the first time from an instrument aboard a sun-synchronous platform. The observed reaction rate is compared to the currently accepted rate determined from laboratory measurements. Good agreement is obtained between the observed and experimental reaction rates down to temperatures as low as 205 K for the first time.

1 Introduction

The importance of N_2O_5 arises mainly from its role as a temporary reservoir for reactive NO_x (NO and NO_2) which catalyse the main ozone-destroying cycles in the stratosphere (Crutzen, 1970). Concentrations of N_2O_5 increase at night and decrease during the day thereby exerting a regulating influence on the rate of ozone destruction throughout the extra-polar stratosphere. The formation of N_2O_5 proceeds at night via the following reactions



where M is any molecule. At sunset, almost all NO is converted rapidly into NO_2 via Reaction (R1). The formation of N_2O_5 then proceeds steadily during darkness hours via a two step process involving Reactions (R2) and (R3), where Reaction (R2) is

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the rate limiting step. The main loss process at night is the thermal decomposition of N_2O_5 , which is the reverse of the three-body reaction in (R3). This process is highly temperature dependent with a time constant of around 3 months at 220 K decreasing to around 30 min at 270 K (Atkinson et al., 2004).

Formation of N_2O_5 is suppressed during the day due to the rapid photolysis of NO_3 . After sunrise, concentrations of N_2O_5 decrease steadily during daylight hours due to photolysis by UV radiation in the range 200–400 nm



where the rate of photolysis depends strongly on the solar zenith angle and the amount of shielding by the overhead ozone column. Loss through thermal decomposition is also ongoing and becomes more important with altitude but is over 10 times slower than the photolytic decay at 40 km and over 100 times slower at 30 km (Connell and Johnston, 1979).

A study by Nevison et al. (1996) assessed the effect of reactions involving ClONO_2 and HNO_3 on diurnal variations in NO_x . At night, the reaction



where M is any molecule is important in the lower stratosphere and tends to increase the sunset/sunrise NO_x ratio. The following reaction which occurs on the surface of sulphate aerosol



is also important in the lower stratosphere where aerosol loading is highest. However, they state that reactions involving ClONO_2 and HNO_3 have little influence on the diurnal NO_x cycle above 35 km.

1.1 Previous measurements

The main aim of this study is to determine the reaction rate controlling the nighttime formation of N_2O_5 given in Reaction (R2) using MIPAS-ENVISAT measurements. While

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reaction rates can be measured in the laboratory, it is always useful to verify that they apply in the real atmosphere, particularly given that the low temperatures and pressures encountered in the stratosphere are difficult to reproduce in a laboratory environment. Although many localised studies have been performed from ground-based or balloon-based experiments, there are very few examples of space-based measurements of rate constants controlling diurnal NO_x chemistry due to the difficulty of following reactions directly given the orbital constraints of the platform.

Highly inclined orbits which precess significantly over time are preferred, as the entire diurnal cycle can be observed on the time scale of days, which allows the diurnal component of variation to be separated from any longer-term seasonal changes, and for reaction rates to be fitted directly to the observations. The chemistry suite on board the Upper Atmosphere Research Satellite (UARS) launched in 1991 allowed the diurnal NO_x cycle to be observed directly from space from a precessing orbit which sampled the diurnal cycle on the time scale of around one month. Two of the atmospheric chemistry instruments on board; the Cryogenic Limb Array Etalon Spectrometer (CLAES) and the Improved Stratospheric and Mesospheric Sounder (ISAMS), were both used to investigate the diurnal NO_x cycle (Kumer et al., 1996; Smith et al., 1996). Although these measurements were able to confirm theoretical predictions about the qualitative behaviour of the diurnal NO_x cycle, the accuracy of the data did not allow for confirmation of the value of key parameters controlling its behaviour, in particular the reaction rates controlling nighttime formation of N_2O_5 and the rate of photolysis of N_2O_5 . This was due in part to the eruption of Mount Pinatubo in 1991 which led to the formation of large amounts of sulphate aerosol in the stratosphere, which on one hand provided a fascinating case study of stratospheric chemistry perturbed by the presence of large amounts of sulphate aerosol, but however added to the inherent problem of distinguishing the weak, continuum-like signal of N_2O_5 from unknown spectral offsets, and so hindered attempts to fully characterise gaseous phase NO_x chemistry.

One of the few space-based observational tests of the parameters used to model the diurnal NO_x cycle was performed by Allen et al. (1990) using a limited number

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of solar occultation measurements performed during the Atmospheric Trace Molecule Spectroscopy (ATMOS) experiment on board Spacelab 3. This was a Shuttle based experiment which used measurements of the NO/NO₂ ratio at sunrise and sunset to evaluate the temperature-dependent rate of Reaction (R2). They concluded that the reaction rate was properly parameterised in current models.

Of the instruments currently in operation, the High Resolution Dynamics Limb Sounder (HIRDLS) on board Aura was originally intended to measure N₂O₅. However, due to the calibration issues arising from the piece of Kapton insulation which came loose upon launch and almost completely blocked the field-of-view, N₂O₅ from this instrument has not yet been used extensively. Apart from HIRDLS, the Atmospheric Chemistry Experiment (ACE) Fourier Transform Spectrometer (FTS), which works by solar occultation, is currently the only instrument other than MIPAS-ENVISAT able to measure N₂O₅ from space. To our knowledge, however, the measurements have so far not been used to determine reaction rates associated with the diurnal NO_x cycle.

In this paper, the rate of Reaction (R2) which regulates the bulk of ozone destruction in the stratosphere (Allen et al., 1990) is determined using data from ESA's Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) instrument on board the sun-synchronous platform Environmental Satellite (ENVISAT). This type of orbit is often considered to be the least favourable, however, due to the perceived complication of separating the diurnal signature from any seasonal variations. However, a single nighttime measurement of N₂O₅, NO₂ and ozone is sufficient to provide an estimate the rate constant controlling the diurnal NO_x cycle which is independent of laboratory parameters used within photochemical models. The MIPAS-ENVISAT measurements of daytime N₂O₅ and ozone as well as nighttime N₂O₅, NO₂ and ozone are used in conjunction with a photolysis model to comment on the rate of photolysis of N₂O₅.

2 MIPAS-ENVISAT

MIPAS-ENVISAT is a high spectral resolution, limb-viewing Fourier transform spectrometer, measuring thermal emission between in five spectral bands (A 685–970 cm^{-1} ; AB 1020–1170 cm^{-1} ; B 1215–1500 cm^{-1} ; C 1570–1750 cm^{-1} ; D 1820–2410 cm^{-1}). The ENVISAT platform is in a sun-synchronous polar orbit at an altitude of around 800 km providing around 1000 spectra each day with global coverage. From July 2002 until March 2004 the instrument operated in its full spectral resolution mode (FR 0.0250 cm^{-1} spectral sampling) with scans spaced by approximately 5° in latitude consisting of 17 spectra acquired at altitudes of 6–68 km with 3 km spacing from 6–42 km, 5 km spacing from 42–52 km, 60 and 68 km. In late March 2004, problems developed in the interferometer drive mechanism and the instrument was switched off for several months. Several new measurement modes were introduced in January 2005 using a reduced spectral resolution and finer vertical measurement grid. In this study, the analysis has been limited to the full resolution dataset in order to avoid complications due to systematic differences between the various measurement modes that are still not fully characterised.

3 Retrievals

N_2O_5 is not one of the standard ESA products retrieved from MIPAS (Raspollini et al., 2006). Therefore, retrievals of N_2O_5 , as well as NO_2 and ozone were performed using the Oxford-based MIPAS Orbital Retrieval using Sequential Estimation (MORSE) algorithm (Dudhia, 2008) with MIPAS version 4.61/4.62 FR L1B spectra. The MORSE algorithm is based on optimal estimation (Rodgers, 2000) and uses prior information about the expected profile to constrain the retrieved values. The a priori volume mixing ratio (VMR) profiles were derived from a climatological database by Remedios et al. (2007) and consist of a mean value that does not include any diurnal variation. To ensure that the influence of the a priori estimate was acceptably small, retrieved values

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in interfering species, instrument calibration uncertainties, the horizontal temperature gradient, and uncertainties in the spectroscopic database. Details of these calculations can be found in Dudhia et al. (2002). The total error budget in this altitude range was found to be 1.7–1.9 K for temperature, 7.2–13.9% for NO₂, 7.5–17.1% for N₂O₅, and 9–10% for ozone. Significant averaging of the data is performed in this study and so the random component can be ignored leaving the systematic component which was found to account for 0.9–1.2 K for temperature, 5.4–8.0% for NO₂, 4.4–7.4% for N₂O₅, and 4.4–7.0% for ozone.

4 Determination of the reaction rate

4.1 Laboratory measurements

The rate of Reaction (R2) used inside stratospheric chemical models is usually calculated using the Arrhenius expression for 2nd order reactions. The Arrhenius expression depends exponentially on temperature and contains two experimentally determined parameters listed in DeMore et al. (1997)

$$k(T) = A \exp\left(\frac{-E}{RT}\right) \quad (1)$$

where k is in units of molecule⁻¹ cm³ s⁻¹, T is kinetic temperature and R is the molar gas constant. As summarised in DeMore et al. (1997) and Atkinson et al. (2004), the preferred values for the Arrhenius factor ($A=1.2 \times 10^{-13}$ molecule⁻¹ cm³ s⁻¹) and temperature coefficient ($E/R \pm (\Delta E/R) = 2450 \pm 150$ K) are derived from a least squares fit of results from laboratory studies by Davis et al. (1974), Graham and Johnston (1974), and Huie and Herron (1974), which were found to be in excellent agreement in the temperature range examined between 231 and 362 K, see Table 1. The rate constant cited in DeMore et al. (1997) derived from this data is recommended for use at temperatures down to 200 K, such as are commonly observed in the lower stratosphere. However,

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the reaction rate at these low temperatures represents an extrapolation of the experimental data, and the expression has not yet been directly verified at temperatures below the lower limit of the laboratory measurements.

An estimate of the error on the Arrhenius estimate of the rate constant due to experimental uncertainties is cited in DeMore et al. (1997) as

$$f(T) = f(298) \exp\left(\frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{298}\right)\right) \quad (2)$$

where $f(298)=1.15$ and $f(T)$ is a multiplicative factor which gives the upper and lower bounds of k corresponding approximately to one standard deviation.

4.2 Observed values

The aim of this study is to compare the recommended value of the rate constant given by the Arrhenius equation against an estimate derived from MIPAS-ENVISAT measurements which does not depend on any of the laboratory-determined parameters used in Eq. (1). This provides useful evidence in support of the laboratory work, as well as providing an indication of how well the the recommended expression performs at the very low temperatures seen in the stratosphere which are difficult to reproduce in the laboratory. The reaction rate may be derived from MIPAS-ENVISAT measurements using the following expression

$$k_{\text{obs}} = \frac{1}{2[\text{O}_3]t} \ln\left(\frac{2\Delta[\text{N}_2\text{O}_5]}{[\text{NO}_2]} + 1\right); \quad \Delta[\text{N}_2\text{O}_5] = [\text{N}_2\text{O}_5] - [\text{N}_2\text{O}_5]_{\text{set}} \quad (3)$$

where t is the number of hours since sunset of the observation, $[\text{N}_2\text{O}_5]$, $[\text{NO}_2]$ and $[\text{O}_3]$ are the observed nighttime mixing ratios of those species, and $[\text{N}_2\text{O}_5]_{\text{set}}$ is the sunset concentration (Toumi et al., 1991). This estimate will be denoted k_{obs} to distinguish it from the standard value of the reaction rate determined using the Arrhenius equation denoted k . This approach also has the advantage of providing an estimate of the reaction rate for a single set of measurements, without the need to track the

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diurnal changes, which is suited to the limited sampling provided in a sun-synchronous orbit. All quantities in Eq. (3) can be measured directly using MIPAS except the sunset concentration of N_2O_5 . At high latitudes in the winter months, the short days and high solar zenith angle result in weak photolysis of N_2O_5 which can result in a non-negligible residual at sunset. In these situations, the residual N_2O_5 may be calculated using the measured daytime concentration of N_2O_5 in conjunction with photolysis rates derived from the Tropospheric Ultraviolet and Visible Radiation Model (Madronich, 2006). However, at lower latitudes and in summertime estimates, the residual at sunset can be neglected.

The main assumptions behind the derivation of Eq. (3) have already been investigated in some detail by Nevison et al. (1996) through comparisons against photochemical models. These assumptions are that the concentrations of ozone and NO_2 remain constant over the course of the night, that thermal decomposition of N_2O_5 is negligible, that concentrations of NO_3 are in a steady state throughout the night, and that losses of NO_2 to the longer-lived reservoirs HNO_3 and ClONO_2 can be ignored. Using a 1-D model of reactive nitrogen chemistry with 12 relevant reactions, Nevison et al. (1996) concluded that thermal decomposition of N_2O_5 was not significant below 40 km. In agreement with these results, the time constant of thermal decomposition calculated under the conditions observed in this study was found to be much longer than the diurnal timescale in most cases and so can reasonably be ignored. Loss of NO_x to the longer-lived reservoirs HNO_3 and ClONO_2 can also be ignored in many circumstances. In the same study by Nevison et al. (1996), comparisons against the 2-D chemical-radiative-dynamical model by Garcia and Solomon (1994) indicated that the formation of HNO_3 and ClONO_2 over the course of the night was only significant below around 35 km. Overall, their study suggests that k_{obs} can be used to provide an estimate of the reaction rate in mid-stratosphere where thermal decomposition, loss of NO_x to ClONO_2 , and heterogeneous loss to HNO_3 can be ignored. Therefore, in this study the determination of the reaction rate using Eq. (3) is limited to mid-stratospheric measurements at nominal tangent altitudes of 33, 36 and 39 km.

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5 Results

Although an estimate of the reaction rate k_{obs} can be obtained using a single set of measurements using Eq. (3), including many measurements at different times of year and in different latitude bands allows a better comparison of k_{obs} against the accepted rate constant k . In this way a wide range of stratospheric temperatures may be examined to test the parameterisation of the reaction rate. In a sun-synchronous orbit, higher latitudes have a greater spread in the time since sunset of measurements over the changing seasons, with summertime measurements that are close to sunset and wintertime estimates that are much later at night, as shown in Fig. 2. By examining measurements obtained in all seasons at different points during the night, it is possible to separate situations where the assumptions behind Eq. (3) are thought to be good from those situations where the estimates may be less reliable.

5.1 Overview of data

Figure 3 shows the nighttime retrieved values of N_2O_5 , NO_2 , and ozone at 33, 36 and 39 km binned in 10° latitude bands by time since sunset of the observation. The estimated sunset concentrations of N_2O_5 corresponding to each bin are also shown. These sunset values were calculated using the daytime measurements of N_2O_5 in Fig. 4 in conjunction with photolysis rates derived from the Tropospheric Ultra-Violet and Visible (TUV) model (Madronich, 2006) to extrapolate to the sunset value. Since the data shows the nighttime evolution of the components of NO_x across the seasons, with summertime measurements corresponding to observations that are close to sunset and wintertime measurements corresponding to observations that are later at night, it is not possible to attempt to fit the reaction rate controlling the formation of N_2O_5 to the data points directly due to the underlying seasonal variations that are unaccounted for, in particular temperature.

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5.2 Temperature dependence of reaction rate

Instead, in Fig. 5 the temperature dependence of the reaction rate k computed using the Arrhenius expression in Eq. (1) is plotted against the MIPAS observations of the reaction rate k_{obs} calculated using Eq. (3) in 5° temperature bins allowing for a possible non-negligible sunset N_2O_5 concentration. The k_{obs} estimates follow the expected exponential temperature dependence well, with the best agreement at 36 km. A deviation of k_{obs} below k is seen at all altitudes for temperatures above 260 K, as this is where thermal decomposition of N_2O_5 , which was neglected in the formulation of Eq. (3), becomes significant. This results in a slower than anticipated increase in nighttime N_2O_5 , and hence lower apparent k_{obs} . However, there appears to be good agreement at all altitudes for temperatures between 220 and 250 K. At low temperatures, there is agreement down to temperatures in the 210–215 K bin at 33 km and down to temperatures in the 205–210 K bin at 36 km, providing observational evidence in support of the reaction rate at the low end of the recommended range in DeMore et al. (1997).

5.3 The reaction rate by season

In Figs. 6–8, k_{obs} at 33, 36, and 39 km is presented grouped by latitude and time since sunset of the observation, so that measurements taken at the same time of year and location are grouped together, allowing situations where the underlying assumptions in the calculation of k_{obs} are thought to be good to be separated from those situations where the assumption may be less reliable.

As expected, the reaction rate is higher in the warmer summertime atmosphere a long time after sunset and, conversely, the reaction rate is slower in the colder wintertime atmosphere at smaller times since sunset. To aid the analysis of the various biases between k_{obs} and k , estimates of k_{obs} are also presented scaled to a temperature of 245 K using the Arrhenius equation

$$k'_{\text{obs}} = k_{\text{obs}} \exp\left(-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{245}\right)\right) \quad (4)$$

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where T is the measured stratospheric temperature. The close agreement between k'_{obs} and the JPL recommendation for the reaction rate at 245 K in Figs. 6–8 tend to support the conclusion in Allen et al. (1990) that the temperature dependence of the rate constant is properly parameterised in current chemical models.

The discrepancies at long times since sunset and small times since sunset between the observed and laboratory reaction rates in Figs. 6–8 can mostly be explained by considering the various assumptions behind the observational estimates. The results accounting for a possible non-negligible sunset N_2O_5 concentration are shown in the second panel of Figs. 6–8. Results assuming that N_2O_5 is completely photolysed by nightfall and that the sunset concentration is zero are shown in the third panel of each figure. It is interesting to note that where the sunset concentration of N_2O_5 is assumed to be zero, there is slightly better agreement between the observed reaction rate and the recommended rate in the tropical latitude bands and in the spring and autumn high latitude estimates at 2–4 h from sunset. In these cases, the sunset concentration is expected to be negligible. Introducing the photolysis calculations results in a slight downwards trend in the reaction rate at 33 and 36 km, which might point to an underestimation of the photolytic decay of N_2O_5 at these altitudes. The trend depends on altitude and is less apparent at 39 km, which suggests that it may be due to the assumption that the ozone column remains constant over the course of the day, when in fact concentrations decrease, or that the measured ozone column used in the photolysis calculations may be slightly too high. Although it is difficult to separate the effect of the photolysis rate from other effects, in the high latitude wintertime estimates, the inclusion of sunset N_2O_5 does generally improve agreement between the observed reaction rate and the recommended rate, removing the upwards trend at long times since sunset. However, the photolysis rates are also a source of uncertainty and are still not well tested. In the past, photolysis rates have been cited as being too fast due to possible problems with the absorption cross-sections or quantum yields, as was stated in a study by Brühl et al. (2007) as one possible reason for overestimation of the diurnal NO_x cycle by the ECHAM5/MESy1 chemistry climate model with respect to

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the IMK/IAA MIPAS measurements. Other authors have concluded that the photolysis of N_2O_5 may be too slow, as was suggested in a study by Allen et al. (1990), which compared ATMOS data with photochemical model results. This underlines the difficulty of separating the various geophysical factors and laboratory parameters affecting the photolysis rate from the surrounding chemistry.

The final point to note is the slight upwards trend in observed reaction rates shortly after sunset, especially in the 40–50° N/S latitude bands. This is not related to the photolysis calculations since here sunset concentrations are negligible. Warm stratospheric temperatures mean that rates of thermal decomposition of N_2O_5 are high. However, the impact of this approximation should still be small since most observations are at temperatures where the thermal decomposition is slow compared to the time elapsed since sunset. For these measurements, the high bias may result from the use of a mean a priori profile which is higher than the values typically observed under these conditions. Figure 4 shows that the retrieved values of N_2O_5 are less than 1 ppbv at all altitudes examined for these cases. In addition, the retrieval of low VMR performed in log-space can also lead to a high bias. Although retrieval in log-space ensures that unphysical negative values are not retrieved, for species with very low VMR, the asymmetry of the a priori distribution can lead to high biased values even when a very large a priori uncertainty is applied. In summary, values of k_{obs} obtained early in the night may be unreliable but highlight the circumstances under which the N_2O_5 retrieval should be treated with caution.

6 Conclusions

The reaction rate controlling the conversion of reactive NO_x into N_2O_5 at night which regulates the majority of ozone destruction at extra-polar latitudes was determined from MIPAS-ENVISAT measurements. Agreement between the observed reaction rate and the current recommended reaction rate for use in stratospheric chemical modelling was good for observations obtained at mid-stratospheric altitudes between 33 and 39 km for

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temperatures between 205 and 250 K. The results support the JPL recommendation for the rate constant. Overall, these results indicate consistency between the key parameters controlling the diurnal NO_x cycle and the Oxford-based MORSE retrievals of NO₂, N₂O₅, and ozone used in this study.

5 *Acknowledgements.* Funded by the Natural Environment Research Council, UK.

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Table 1. Table summarising main laboratory measurements of $\text{NO}_2 + \text{O}_3 \xrightarrow{k} \text{NO}_3 + \text{O}_2$ adapted from Atkinson et al. (2004). The most recent recommended value of k (DeMore et al., 1997) is based on a least squares fit analysis of the data presented in the first three studies.

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference
$9.76 \times 10^{-14} \exp[-(2427 \pm 140)/T]$	260–343	Davis et al. (1974)
$1.34 \times 10^{-13} \exp[-(2466 \pm 30)/T]$	231–298	Graham and Johnston (1974)
$1.57 \times 10^{-13} \exp[-(2509 \pm 76)/T]$	259–362	Huie and Herron (1974)
$1.2 \times 10^{-13} \exp[-(2450 \pm 150)/T]$	200–300	DeMore et al. (1997)

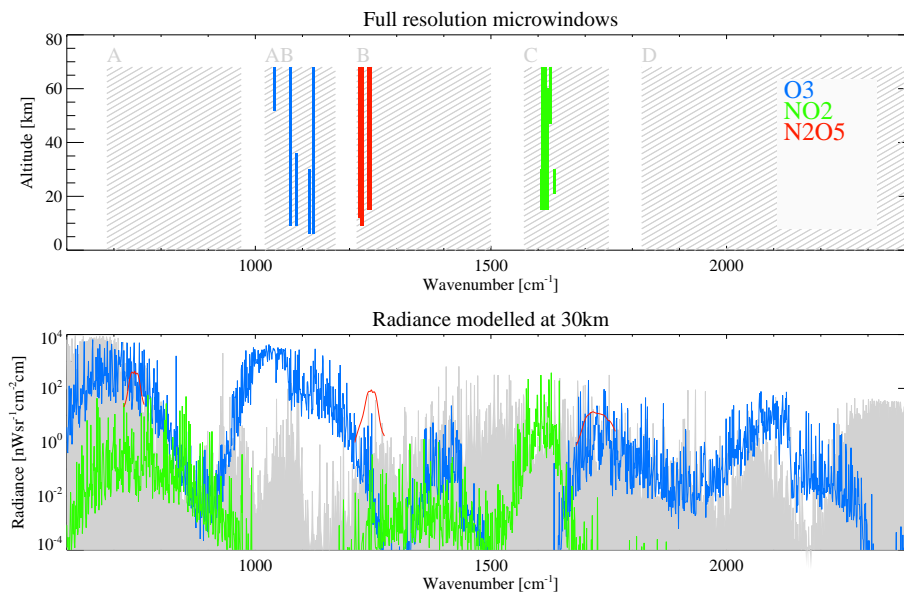
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Fig. 1. Top panel shows spectral regions used to retrieve N_2O_5 in red, NO_2 in green and ozone in blue. Grey shaded area shows bands covered by MIPAS-ENVISAT. Bottom panel shows contribution to modelled limb radiance at 30 km for each species for a standard atmosphere. Contribution of other molecules (mainly water vapour and CO_2) shown in grey.

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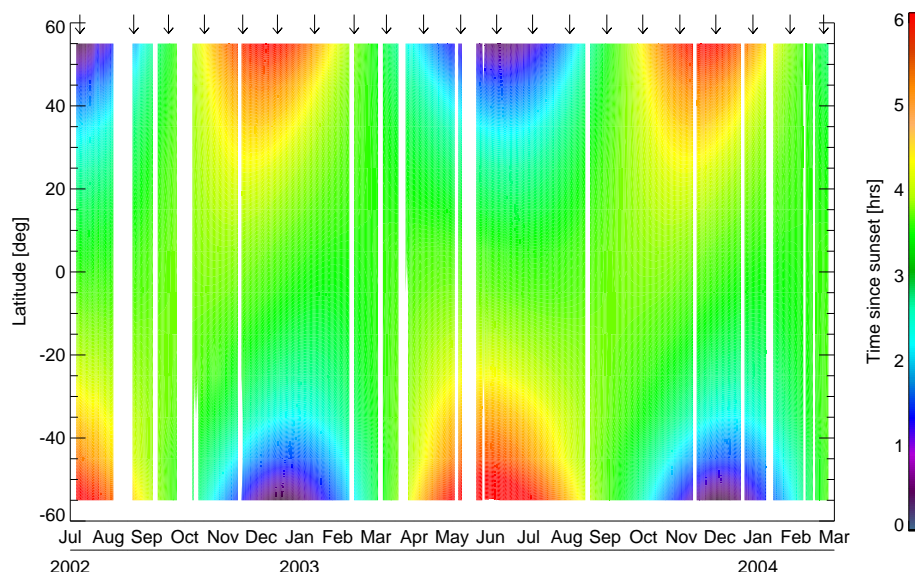


Fig. 2. Seasonal variation in time since sunset of MIPAS-ENVISAT observations. Arrows indicate sample days used to compute the rate constant (9 Jul 2002, 23 Aug 2002, 21 Sep 2002, 21 Oct 2002, 22 Nov 2002, 21 Dec 2002, 21 Jan 2003, 23 Feb 2003, 22 Mar 2003, 22 Apr 2003, 23 May 2003, 22 Jun 2003, 22 Jul 2003, 22 Aug 2003, 22 Sep 2003, 22 Oct 2003, 22 Nov 2003, 22 Dec 2003, 22 Jan 2004, 22 Feb 2004, 22 Mar 2004). White areas indicate where data was unavailable.

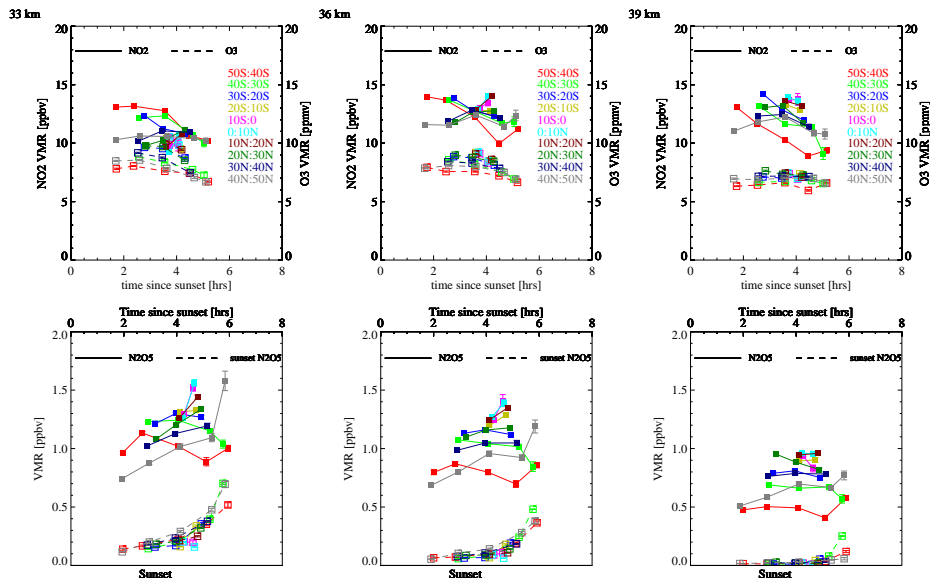
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Fig. 3. Top panel shows measured nighttime concentrations of NO_2 and ozone binned by hour since sunset in 10° latitude bands where $50\text{--}40^\circ\text{S}$ shown in red, $40\text{--}30^\circ\text{S}$ in light green, $30\text{--}20^\circ\text{S}$ in dark blue, $20\text{--}10^\circ\text{S}$ in yellow, $10\text{--}0^\circ\text{S}$ in pink, $0\text{--}10^\circ\text{N}$ in pale blue, $10\text{--}20^\circ\text{N}$ in maroon, $20\text{--}30^\circ\text{N}$ in dark green, $30\text{--}40^\circ\text{N}$ in navy blue, and $40\text{--}50^\circ\text{N}$ in grey. Bottom panel shows measured concentrations of N_2O_5 at the given time since sunset (upper axis), and the N_2O_5 concentration at sunset modelled using the TUV for the given bin. Error bars indicate error in mean.

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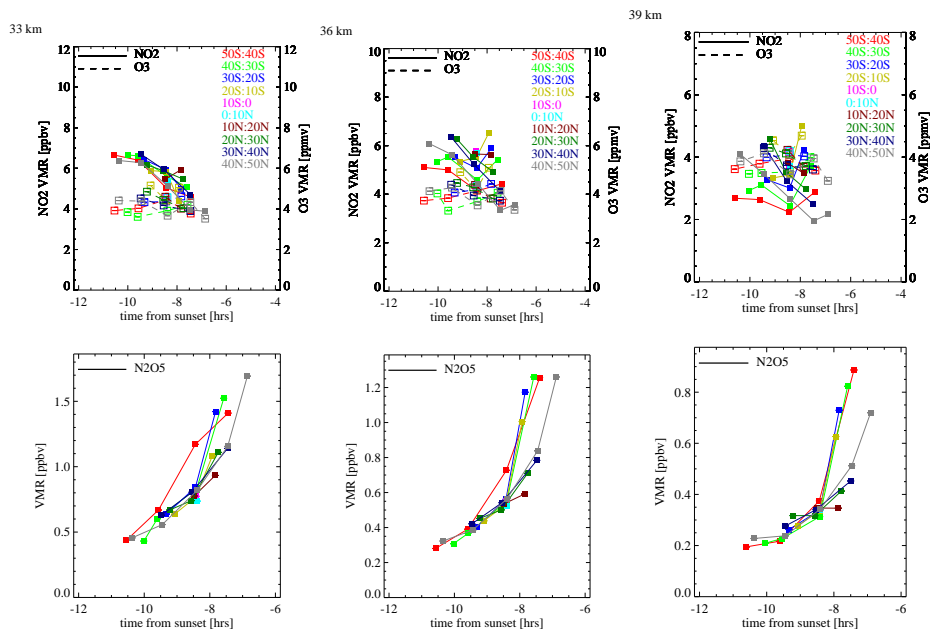
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Fig. 4. Top panel shows measured daytime concentrations of ozone and NO_2 binned by hour from sunset in 10° latitude bands where 50–40° S shown in red, 40–30° S in light green, 30–20° S in dark blue, 20–10° S in yellow, 10–0° S in pink, 0–10° N in pale blue, 10–20° N in maroon, 20–30° N in dark green, 30–40° N in navy blue, and 40–50° N in grey. Lower panel in each figure shows daytime observations of N_2O_5 binned in the same way. Error bars indicate error in mean.

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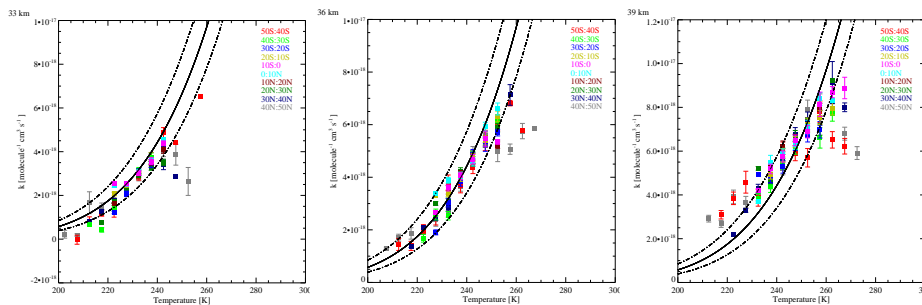
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Fig. 5. Temperature dependence of rate constant determined at tangent altitudes of 33, 36, and 39 km using $k_{\text{obs}} = \frac{1}{2[\text{O}_3]t} \ln \left(\frac{2\Delta[\text{N}_2\text{O}_5]}{[\text{NO}_2]} + 1 \right)$ in Eq. (3) assuming possible non-negligible N₂O₅ at sunset binned in 5 K temperature increments in 10° latitude bands where 50–40° S shown in red, 40–30° S in light green, 30–20° S in dark blue, 20–10° S in yellow, 10–0° S in pink, 0–10° N in pale blue, 10–20° N in maroon, 20–30° N in dark green, 30–40° N in navy blue, and 40–50° N in grey compared against the temperature dependence computed using Arrhenius expression $k(T) = A \exp\left(\frac{-E}{RT}\right)$ in Eq. (1).

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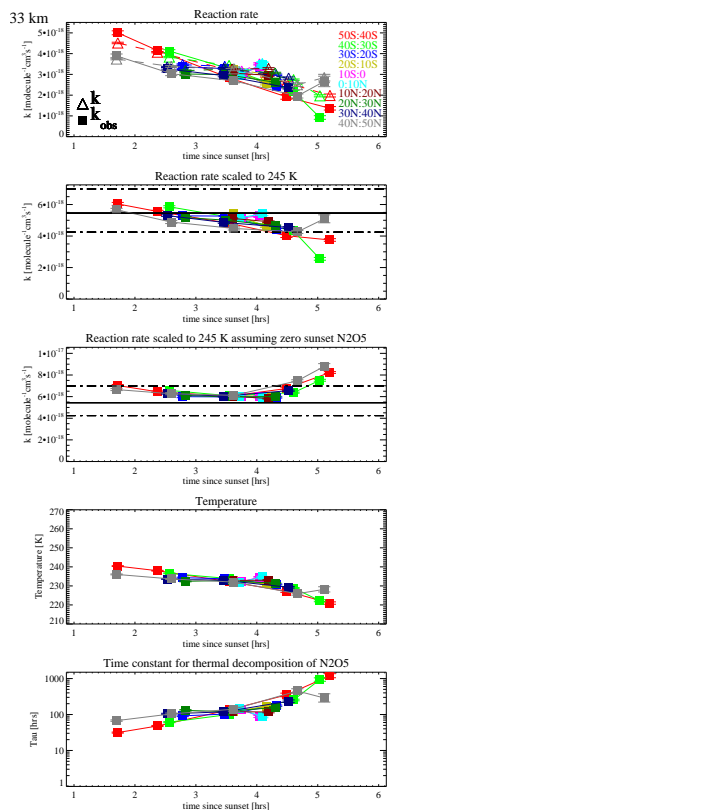
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Fig. 6. Results of analysis presented by season at 33 km. Top panel shows k_{obs} and Arrhenius k (computed for observed atmospheric temperature) binned in 10° latitude bands where 50–40° S shown in red, 40–30° S in light green, 30–20° S in dark blue, 20–10° S in yellow, 10–0° S in pink, 0–10° N in pale blue, 10–20° N in maroon, 20–30° N in dark green, 30–40° N in navy blue, and 40–50° N in grey, grouped also by hour since sunset. Second panel shows k_{obs} scaled to the value it would assume at 245 K where the residual sunset N_2O_5 has been estimated using the TUV. Third panel is as in second panel except sunset N_2O_5 concentrations are assumed to be negligible. Fourth panel shows the measured atmospheric temperature. Fifth panel shows an estimate of the time constant of the thermal decomposition of N_2O_5 calculated considering the measured temperature and pressure.

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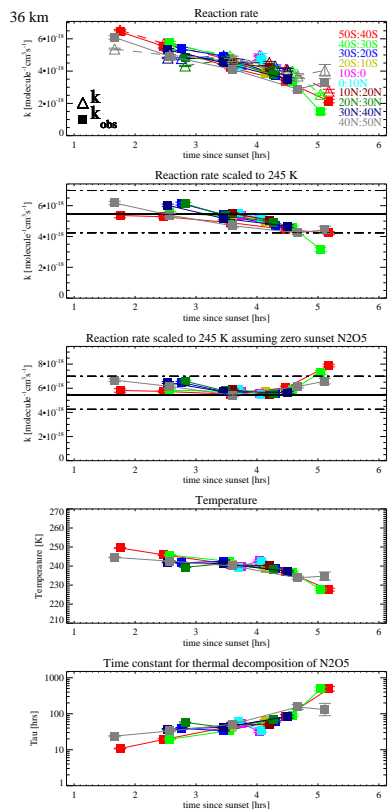


Fig. 7. As in Fig. 6 but at 36 km.

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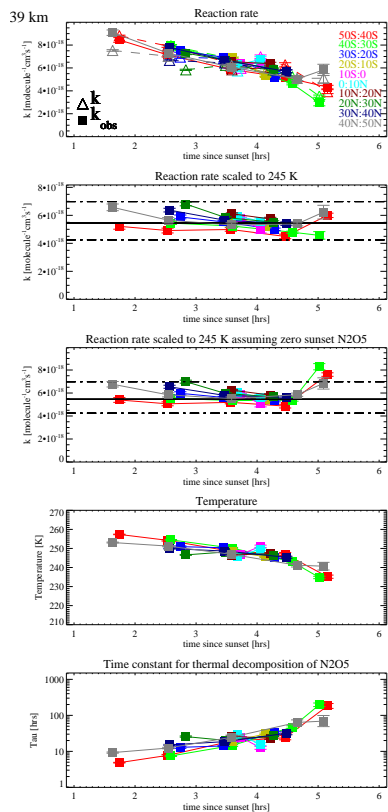


Fig. 8. As in Fig. 6 but at 39 km.

