

# ***Interactive comment on “Measurement from sun-synchronous orbit of a reaction rate controlling the diurnal NO<sub>x</sub> cycle in the stratosphere” by J. C. Walker and A. Dudhia***

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## **1 Replies to general comments**

We thank the reviewer for their comments which we have found very useful. In response to the general comment that “*the authors could be more quantitative without much additional work*”, the authors are in agreement and the referee’s suggestions outlined in comment 3 are included in the amended manuscript.

The authors accept that the references on stratospheric nighttime NO<sub>x</sub> chemistry are somewhat dated and have updated the literature review with the suggested studies

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performed over the past decade using the GOMOS instrument on board ENVISAT.

## 2 Replies to specific comments

1. In response to Referee #1's comment "*To ensure that the influence of the a priori estimate was acceptably small, retrieved values with an a priori contribution of greater than 50% were removed from the analysis.*" I am no specialist. What would happen in the cases when the a priori is excellent reproducing more or less the reality and so matching the retrieved value? Would the contribution of the a priori be greater than 50 percent?", the authors reply that extremely reliable a priori data is not available. The prior data for the species retrieved in this study have a large uncertainty for the time and location of any particular observation. This is especially the case since the species are also diurnally varying, meaning that prior data has an even larger error bar. Therefore, the a priori uncertainty was assumed to be large and was assigned a value of 100% of the profile value. This prior data is needed to invert the spectral measurements successfully when the spectral signature is weak due to the problem of ill-conditioning. When the spectral data contributes significant new information, the random error on the retrieved profile should be significantly lower than the random error assigned to the a priori profile. As a rough rule of thumb, from consideration of the combination of scalar measurements, a 70 % retrieval random error with a prior error of 100% implies that 50 % of the information is coming from the spectral data rather than the a priori. In this study, we imposed a somewhat stricter condition that the random error had to improve from an a priori error of 100 % to a retrieval error of 50 % for the data to be used to estimate  $k$ , to avoid possible bias introduced by including retrievals that had been heavily influenced by the prior data. However, in the hypothetical case of very accurate a priori data, then the a priori error assigned would be smaller, and in those circumstances, a trusted prior

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- could contribute more than the spectral measurements. However, in reality, the climatological data is not thought to be that accurate.
2. In response to Referee # 1's comments that '*Very surprisingly, the authors do not mention and discuss previous studies devoted to the same topic (full checking of the stratospheric nighttime NO<sub>x</sub> chemistry and associated rate constants; estimation of the rate constant of NO<sub>2</sub>+O<sub>3</sub> rate) using a similar methodology (satellite chemical measurements and chemistry arguments) (see Marchand et al., GRL, 2004 et 2007)*', we have included a review of the results in the amended paper.
  3. In response to Referee #1's comments that '*The authors compare chemical observations and theoretical calculations to conclude that the JPL value for the NO<sub>2</sub>+O<sub>3</sub> rate constant is consistent with the observations. But how consistent? They can try to be more quantitative and go one step further. They can derive the value of the rate constant that fits best (in the least-square sense) their chemical observations using minimisation techniques. They can then compare their estimate (with uncertainties represented by the standard deviations) with the JPL value and uncertainties.*', we have implemented this suggestion in the revised manuscript, and have derived the pre-exponential factor and activation energy associated with the reaction rate from the MIPAS measurements in the least-squares sense using minimisation techniques as suggested. The results are summarised in the attached table. The results indicate agreement within the error bar for the estimate of  $k$  at temperature 245 K, although the fitted parameters in the Arrhenius expression are somewhat different, but as shown in the attached figures result in curves within the JPL error bounds for the reaction rate in the stratospheric temperature range.

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		$A/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$(E/R)/\text{K}$	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 245 K	Temp/K
JPL		$1.4 \times 10^{-13}$	$2470 \pm 150$	$(5.4^{+1.5}_{-1.3}) \times 10^{-18}$	230-360
MIPAS	33 km	$(3.2 \pm 0.3) \times 10^{-13}$	$2708 \pm 18$	$(5.0 \pm 0.5) \times 10^{-18}$	200-250
	36 km	$(20.1 \pm 2.6) \times 10^{-15}$	$2028 \pm 30$	$(5.1 \pm 0.9) \times 10^{-18}$	205-250
	39 km	$(14.3 \pm 2.4) \times 10^{-15}$	$1914 \pm 38$	$(5.8 \pm 1.3) \times 10^{-18}$	210-250

**Table 1.** Table summarising the MIPAS observations of  $k$  in comparison to the JPL recommendation for reaction  $\text{NO}_2 + \text{O}_3 \xrightarrow{k} \text{NO}_3 + \text{O}_2$ . The values for the pre-exponential parameter ( $A$ ) and the activation energy ( $E/R$ ) are derived from the data shown in the attached figures. The value of the reaction rate at 245 K agrees in all cases.

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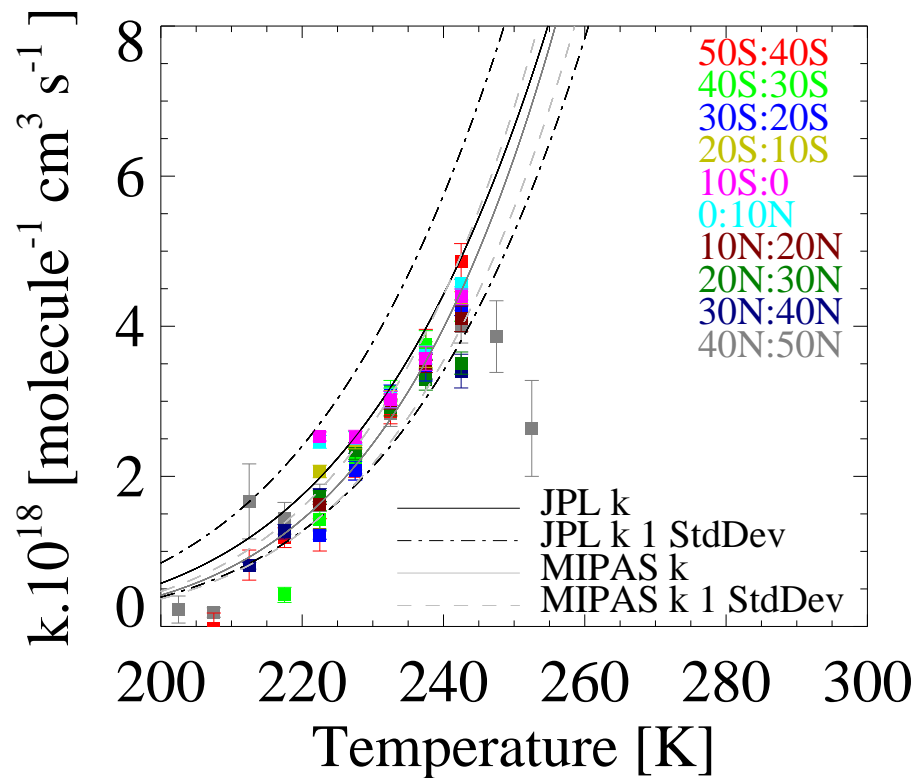
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Fig. 1.

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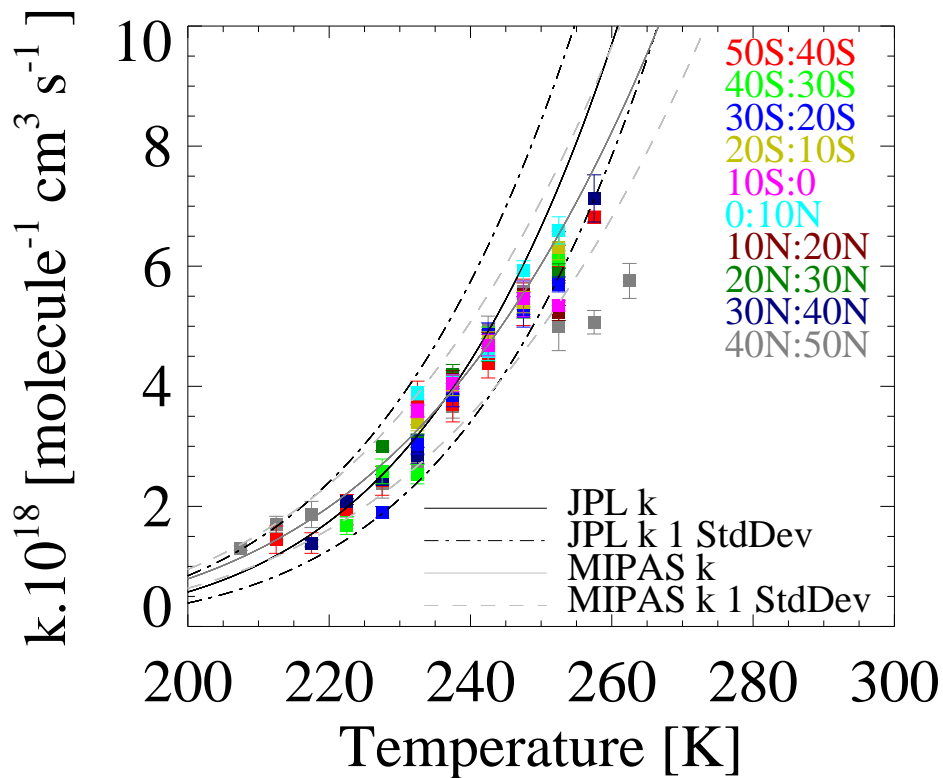
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Fig. 2.

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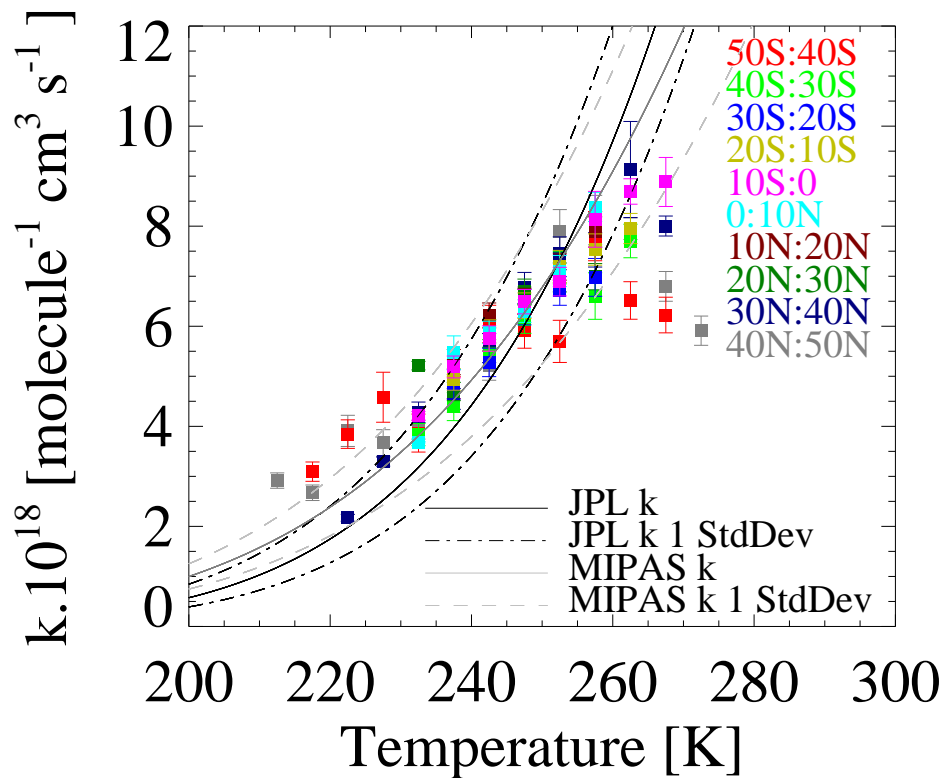
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Fig. 3.

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