Inferring the Photolysis Rate of NO₂ in the Stratosphere
Based on Satellite Observations

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Abstract. NO and NO₂ (NOx) play major roles in both tropospheric and stratospheric chemistry. This paper provides a novel method to obtain a global and accurate photodissociation coefficient for NO₂ based on satellite data. The photodissociation coefficient J₉0₂ dominates the daytime diurnal variation of NOx photochemistry. Here the spatial variation of J₉0₂ in 50° S-90° S in December from 20-40 km is obtained using data from the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) experiment. Because NO and NO₂ exchange rapidly with one another in the daytime, the J₉0₂ can be attained assuming steady state, and the results are shown to be consistent with model results. The J₉0₂ value decreases as the solar zenith angle increases and has a weak altitude dependence. A key finding is that the satellite-derived J₉0₂ increases in the polar regions in good agreement with model predictions, due to the effects of ice and snow on surface albedo. Thus, the method presented here provides an observations-based check on the role of albedo in driving polar photochemistry.

1 Introduction

Fast photochemistry in the Earth’s atmosphere is driven by sunlight and affects the diurnal variation of many species. The properties of sunlight entering the stratosphere, including light intensity and its energy distribution, depend on the solar zenith angle, as well as the overhead concentrations of oxygen and ozone and the reflective properties of the underlying troposphere. Further, the solar zenith angle is related to latitude, season, and local time. The sunlight entering the stratosphere determines the photochemical rates in the stratosphere, thus affecting stratospheric chemistry, and the diurnal variations of species concentration is one of the impacts. Therefore, diurnal variation observations provide key information in analyzing the photochemical properties of the stratosphere. NOx chemistry is one of the most important elements of stratospheric chemistry and plays a leading role in controlling stratospheric ozone concentration (Crutzen, 1979; Johnston, 1971; Crutzen, 1970). The photodissociation coefficient J₉0₂ quantifies the process of NO₂ photolysis into NO, thus affecting the diurnal variation of NOx. The stratospheric NO and NO₂ abundances are controlled by the following reactions:

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R1)} \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \quad \text{(R2)} \\
\text{NO}_2 + \text{O} & \rightarrow \text{NO} + \text{O}_2 \quad \text{(R3)} \\
\text{ClO} + \text{NO} & \rightarrow \text{NO}_2 + \text{Cl} \quad \text{(R4)}
\end{align*}
\]

Because of the short lifetime of NO and NO₂, they are in steady state within the sunlit stratosphere. Therefore, the following equation holds:
A number of studies on the diurnal variation of NOx and J_{NO2} in the stratosphere have been reported, based on models or airborne observations. Fabian et al. (1982) used a two-dimensional model to examine the diurnal variations of NOx at different altitudes. Many studies of the NOx diurnal variation based on airborne observations which were then compared with models (Pommereau, 1982; Roscoe et al., 1986; Kawa et al., 1990). Madronich et al. (1985) measured J_{NO2} in the stratosphere utilizing a balloon platform and compared it to a model; they showed that the J_{NO2} value has a weak altitude dependence. Webster and May (1987) measured the diurnal variation of NOx and J_{NO2} simultaneously utilizing a balloon. Del Negro et al. (1999) calculated J_{NO2} based on the concentrations of NO, NO2, O3, ClO, and HO2 measured on an aircraft and BrO from a model, and compared them with a model. They found that the J_{NO2} inferred from the data assuming steady state matched their model well. Moreover, it has been emphasized that albedo has a substantial effect on J_{NO2} (Madronich, 1987; Bösch et al., 2001; Laepple, 2005; Walker et al., 2022). Further, the surface albedo over ice and snow has a large and important effect on tropospheric chemistry in the polar regions (Walker et al., 2022) due in large part to its effect on J_{NO2}, highlighting the need to evaluate J_{NO2} on a large scale. Surface radiometers have also been used to infer information about J_{NO2} for different sky conditions in the troposphere (Shetter et al., 1992; Junkermann et al., 1989). However, aircraft, surface radiometers, or balloon measurements are all local and the amount of data is therefore limited. At the same time, models are based on theoretical calculations and require measured data for verification. These considerations are the motivation for this paper, in which satellite data are used to characterize J_{NO2} on a global basis, with particular emphasis on values obtained over ice and snow.

Satellite measurements of NOx allow elucidation of its zenith angle and albedo dependence. The global concentrations of NO, NO2, and related species as discussed below can be easily obtained using satellite data and used to determine J_{NO2} at different latitudes, albedo, and altitudes. Solomon et al. (1986) reported satellite observations of the NO2 diurnal variation in the stratosphere at solar zenith angles ranging from about 35 to 110 degrees but concurrent NO data were not available. Anderson et al. (1981) employed a similar method to study the zenith angle variation of mesospheric O3. The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a backscatter Fourier transform spectrometer carried on Envisat, measuring not only NO2 but also NO and O3, as well as ClO, all of which are used here in inferring J_{NO2} (see below). MIPAS was designed and operated for the measurement of atmospheric species from space and can detect limb emission in the middle atmosphere with high spectral resolution and low-noise performance (Fischer et al., 2008).

In this work, the novel method of obtaining the zenith angle dependence of NOx and J_{NO2} using satellite data in summer over the polar cap is reported, taking 50° S-90° S in December in 20-40 km as an example. The diurnal variations of NOx and J_{NO2} at different altitudes are described. J_{NO2} changes with latitude are discussed and a J_{NO2} map in the Antarctic is used to elucidate albedo effects. In summary, this work shows a method for obtaining NOx diurnal variation and accurate J_{NO2} based on satellite data, expanding the way to attain information on this key photodissociation coefficient.

2 Data and Methods

2.1 MIPAS Data

The vertical resolution of MIPAS is approximately 3 km and the horizontal resolution of MIPAS is 30 km, and the vertical scan range is 5-150 km. Satellite operation was stopped temporarily in March 2004 due to technical issues and resumed in January 2005 in a new operation mode. MIPAS allows near complete global coverage, ranging from 87° S to 89° N obtained about every three
days by 73 scans per orbit and 14.3 orbits per day. Each day the satellite passes through the same latitude at two local times (ascending side and descending side, as shown in Fig. 1). Therefore, for this dataset, there are only two solar zenith angles at each latitude. We therefore focus on 50° S-90° S in the polar day, in December 2009, where there are as many solar zenith angles as possible in a relatively small latitude range. In this paper, the NO, NO$_2$, O$_3$, ClO, temperature and pressure data were from V8 level 2 MIPAS retrievals (Kiefer et al., 2021, 2022). The reported precision between 20 km and 40 km is 5-15 % for NO (Funke et al., 2022; Sheese et al., 2016), 5-15 % for NO$_2$ (Wetzel et al., 2007), 2-3 % for O$_3$ (Laeng et al., 2015) and more than 35 % for ClO (Von Clarmann et al., 2009).

![Figure 1. Schematic representation of the MIPAS orbit at high latitude in December showing the ascending (dayside) and descending (nightside) portions of the orbit and the terminator.](https://doi.org/10.5194/egusphere-2023-557)

2.2 Model Calculations

The Whole Atmosphere Community Climate Model version 6 (WACCM6) is used in this study. WACCM6 is a component of the Community Earth System Model version 2 (CESM2; Gettelman et al., 2019; Danabasoglu et al., 2020). The horizontal resolution is 1.9° latitude × 2.5° longitude and the with 88 vertical levels up to about 140 km, with the altitude resolution increasing from 0.1 km near the surface to 1.0 km in the upper troposphere–lower stratosphere (UTLS) and 1–2 km in the stratosphere. This work uses the specified dynamics version of WACCM6, where the atmosphere below 50 km is nudged to the Modern-Era Retrospective Analysis for Research and Applications, version 2 (MERRA-2; Gelaro et al., 2017), temperature and wind fields with a relaxation time of 50 h. The chemistry mechanism includes a detailed representation of the middle atmosphere, with a sophisticated suite of gas-phase and heterogeneous chemistry reactions, including the Ox, NOx, HOx, ClOx, and BrOx reaction families. There are ~100 chemical species and ~300 chemical reactions. Reaction rates are updated following Jet Propulsion Laboratory (JPL) 2015 recommendations (Burkholder et al., 2015). The photolytic approach is based on both inline chemical modules (<200nm) and a lookup table approach (>200-750nm; see Kinnison et al., 2007). The look-up table (LUT) approach uses the Tropospheric Ultraviolet-Visible Radiation Model (TUV4.2; Madronich, 1987; Madronich and Weller, 1990), an advanced radiation transfer model widely used by the scientific community, using the four-stream pseudospherical discrete ordinates option. Model values for December 2009 at the same times and location as the satellite data are selected to compare with the satellite data, and denoted “Model”.

2.3 Chemical Equation

NO is assumed to be in a steady state in the sunlit atmosphere at 20-40 km at least for a zenith angles less than 94°, due to its short lifetime. Using the chemistry discussed above, $J_{NO_2}$ can then be expressed as
\[ J_{\text{NO}_2} = \frac{[\text{NO}]}{[\text{NO}_2]} \times \left( k_{\text{NO}+\text{O}_3} \times [\text{O}_3] + k_{\text{NO}+\text{ClO}} \times [\text{ClO}] \right) - k_{\text{O}+\text{NO}_2} \times [\text{O}] \]  

(2)

Where \( k \) is the rate constant, \( J_{\text{NO}_2} \) is the photodissociation coefficient of \( \text{NO}_2 \), and \([\text{O}_3]\) is the concentration of \( \text{O}_3 \).

To obtain the concentration of \( \text{O} \), \( \text{O} \) is assumed to be in a steady state with ozone at 20–40 km. The concentration of \( \text{O} \) can be expressed as

\[ [\text{O}] = \frac{J_{\text{O}_3} \times [\text{O}_3]}{k_{\text{O}+\text{NO}_2} + [\text{O}_3] [\text{M}]} \]  

(3)

It is worth noting that \( J_{\text{O}_3} \) in the Eq. (3) comes from the model here, which is a limitation of this study. However, in the stratosphere below about 33 km \([\text{O}]\) has a small effect on \( J_{\text{NO}_2} \) (less than 8.1 percent). \( \text{ClO} \) can similarly be ignored when altitudes are less than 35 km, where \( \text{ClO} \) concentrations are small; otherwise using \( \text{ClO} \) data from MIPAS would introduce large and unnecessary uncertainty. \( \text{HO}_2 \) and \( \text{BrO} \) both can react with \( \text{NO} \) but they are not measured by MIPAS and their contributions to the partitioning between \( \text{NO} \) and \( \text{NO}_2 \) are negligibly small at the altitudes considered here. Therefore, we don’t consider them in this paper.

3 Results and Discussion

3.1 NOx Concentration at different altitudes

To better understand the diurnal variation of NOx, concentrations of \( \text{NO} \) and \( \text{NO}_2 \) from MIPAS and the model are shown in Fig. 2 at different altitudes. The \( \text{NO} \) and \( \text{NO}_2 \) concentrations from MIPAS and the model show very good overall consistency. The solar zenith angle of 90 degrees is a clear dividing line, showing that light drives the diurnal variation, and the results are in good accord with the theory.
Figure 2. The concentrations of NO, NO₂ and NOₓ in 50° S-90° S in December 2009 from MIPAS and the model at different altitudes. (a) 23 km (b) 28 km (c) 33 km (d) 38 km. Model values are at the same time and location as the satellite data. The color bar represents the latitude of the data points at each solar zenith angle. Each point represents the four-day running mean of the average concentration of multiple daily measurements at two latitude degree intervals.
NO and NO₂ exchange with one another but their sum (NOx) varies relatively little for solar zenith angles less than about 90°. An increase in NO is matched by a decrease in NO₂ for zenith angles from about 30°-50°, and then decreases at larger angles, mainly reflecting changes in the photolysis rate as the satellite sweeps across the mid-latitudes and polar cap (see below). NO rapidly disappears when the solar zenith angle exceeds 90 degrees, so the concentrations of NO and NO₂ change dramatically during twilight. NO decreases rapidly and NO₂ increases rapidly. When the solar zenith angle is more than 90 degrees at these altitudes, NO is completely oxidized to NO₂, so there is no NO and NO₂/NOx is 1. In addition, the concentration of NO₂ decreases when the solar zenith angle is more than 90 degrees, which indicates the formation of the N₂O₅.

It should also be noted that in Fig. 2, the concentrations of NO and NO₂ also reflect latitude variations, because the data at each zenith angle come from different latitudes as shown by the color bar at the top of each panel in Fig. 2, but these variations are fairly small over the summer polar cap and consistent with the model as shown. From 23 km to 33 km, the concentrations of NO and NO₂ increase with the altitude.

3.2 \( J_{NO_2} \) at different altitudes and solar zenith angles

Using Eq. (2) above, the \( J_{NO_2} \) at different altitudes is shown in Fig. 3 along with the calculated \( J_{NO_2} \) values from the model. The correlation diagrams show that the values inferred from the satellite observations are in excellent agreement with the model. Fig. 3 shows that from 20-40 km, the \( J_{NO_2} \) values at different altitudes are nearly the same. This indicates the weak dependence of \( J_{NO_2} \) value on altitude, which was also reported by Madronich et al. (1985). This is because the NO₂ photolysis is largely driven by wavelengths ranging from 300 nm to 420nm (Madronich et al., 1983). This spectral region is relatively free of atmospheric absorption, so the flux is nearly the same at different altitudes. When the solar zenith angle is higher than about 90 degrees, the \( J_{NO_2} \) value drops rapidly to 0. To illustrate how different species affect our calculations at some altitudes, the effects of different gases at 38 km are shown in Fig. S1. The figure shows that O₃, O and ClO are critical to NOx chemistry at 38 km. However, the concentrations of ClO and O are smaller at altitudes of less than 35 km, and have about 3.6% and less than 12% influence in our calculations, respectively. Moreover, the satellite data error of ClO becomes large at lower levels, so ClO is not considered here when the altitude is lower than 35 km.
Figure 3. The JNO$_2$ in 50° S-90° S from MIPAS and the model at different altitudes. (a) 23 km (b) 28 km (c) 33 km (d) 38km. Model values are for the same time and location as the satellite data. The color bar represents the latitude of the data points at nearly the same solar zenith angle. Each point in JNO$_2$-Model and JNO$_2$-MIPAS represents the four-day running mean of the average JNO$_2$ of multiple daily measurements at two latitude degree intervals. In the correlation plots, the abscissa is JNO$_2$-MIPAS and the ordinate is the JNO$_2$-Model and the slope of dashed line is 1.

3.3 JNO$_2$ at different latitudes

The JNO$_2$ values from the satellite and model at different latitudes are next discussed. The clear relationship between JNO$_2$ and latitude from MIPAS and model is also displayed in Fig. 4, and the close comparison between the two is remarkable. It is obvious that the satellite-inferred JNO$_2$ monotonically increases with latitude from 30° S-70° S, and then decreases at higher latitudes. The JNO$_2$ over the pole is taken at a larger solar zenith angle, which explains its decrease relative to surrounding parts of Antarctica. Fig. 5 displays maps of the detailed distributions of JNO$_2$ from MIPAS and model, which exhibits their excellent consistency and shows a sharp transition between mid-latitudes and the Antarctic continent or regions covered by sea ice.
The sharp transitions in $J_{NO_2}$ values shown in Fig. 5 can only be caused by the large difference in albedo between the ocean and the Antarctic environs, covered by sea ice, land ice, and snow (Brandt et al., 2005; Shao and Ke, 2015). Albedo has a strong influence on $J_{NO_2}$ because NO$_2$ is more sensitive than most atmospheric species to the effects of scattering and reflection (Madronich et al., 1983; Madronich, 1987; Bösch et al., 2001; Laepple et al., 2005). In the high latitude area, the ground is covered with ice and snow, and the albedo can be as high as 0.9, while in the lower latitudes, the albedo is about 0.1 (Brandt et al., 2005; Shao and Ke, 2015). Table 1 shows the $J_{NO_2}$ values at different solar zenith angles under different albedos. The results show that the albedo has a strong influence on the values, especially at low solar zenith angles. Based on Fig. 5, the $J_{NO_2}$ above the continental ice is greater than that above the Antarctic sea ice, which may be because the fraction of open water within the pack influences the albedo (Brandt et al., 2005).

![Graph showing the relationship between $J_{NO_2}$ and latitude from MIPAS and model in 30° S-90° S at 28 km. Model data are for the same time and location as the satellite data. $J_{NO_2}$ is examined wherever the solar zenith angle is less than 70 degrees and averaged every five degrees of latitude.](https://doi.org/10.5194/egusphere-2023-557)
Figure 5. The mapping of $J_{NO_2}$ in 50° S-90° S at 28 km from (a) MIPAS and (b) model. (c) The distribution of the sea ice extent in December, 2009 in Antarctica and its albedo, from the model. Model $J_{NO_2}$ data are for the same time and location as the satellite data. $J_{NO_2}$ is shown wherever the solar zenith angle is less than 70 degrees and averaged every 3.33° latitude $\times$ 15° longitude.

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<th>Solar zenith angle</th>
<th>$J_{NO_2}$ ($\alpha = 0.1$)</th>
<th>$J_{NO_2}$ ($\alpha = 0.9$)</th>
<th>$J_{NO_2}$ ($\alpha = 0.9$)/$J_{NO_2}$ ($\alpha = 0.1$)</th>
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4 Conclusions

The diurnal variations of NOx species and the resulting $J_{NO_2}$ from about 50° S-90° S in December in 20-40 km have been evaluated based on MIPAS data. Light has a strong impact on the diurnal variations. NO and NO$_2$ are in steady state in the daytime and their sum is almost constant.
The calculated $J_{NO_2}$ remarkably consistent with the model results, and the $J_{NO_2}$ value decreases as the solar zenith angle increases.

The $J_{NO_2}$ value drops rapidly to 0 at the solar zenith angle of about 90 degrees. Moreover, the weak dependence of the $J_{NO_2}$ value on altitude in this region is evident.

The results from the satellite and the model both indicate that $J_{NO_2}$ increases with latitude, which can be attributed to more reflected light from ice and snow surfaces with high albedo. In summary, this work presents a new method for obtaining accurate $J_{NO_2}$ values based on satellite data. Further, this method can be extended to other photodissociation coefficients, paving the way for further tests of global photodissociation coefficients data based on satellites.

**Code and data availability.** The data and code are available at https://doi.org/10.5281/zenodo.7764756.

**Supplement.**

**Author contributions.** S.S. designed the study. J.G. analyzed the data and produced the figures. S. M. and D. K. run the models and contributed significantly to the interpretation of findings. J.G. wrote the manuscript, with comments from all authors.

**Competing interests.** The contact author has declared that none of the authors has any competing interests.

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