ABSTRACT

NO, NO2, and N2O play a central role in stratospheric chemistry. We use MORSE, (MIPAS Orbital Retrieval using Sequential Estimation), to retrieve NO2 and N2O. Significant improvements are made to the N2O retrieval by retrieving a single value for the aerosol continuum across the N2O emission feature. Performing a retrieval of NO is complicated by Non-LTE effects. Instead, we infer NO concentrations using diurnal NOx conservation and compare NO estimates with the IMK-IAA Non-LTE retrieval. Through consideration of time since sunnset, rate constants for diurnal NOx interconversion are determined.

MIPAS

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a limb viewing fourier transform spectrometer aboard ENVISAT. It operates in the near to mid-infra-red where many important species affecting the chemical and radiative properties of the atmosphere have characteristic emission features. The MORSE retrieval algorithm uses an optimal estimation approach, (Rodgers, 2000). The forward model used is the RPM, (Reference Forward Model), which is a line by line radiative transfer code.

MICROWINDOWS

Retrievals are performed using small sections of the spectrum, known as microwindows, which maximise information content and minimise systematic and random errors for the target molecule.

IMPROVEMENTS TO N2O RETRIEVAL

The spectral signature of N2O resembles that of the aerosol continuum. For an accurate retrieval, NO2 needs to be retrieved jointly with aerosol. Simulated joint retrievals showed precision was significantly improved by retrieving a single value for aerosol across the entire spectral region, rather than retrieving a different value for aerosol in each microwindow.

RESULTS OF NO ESTIMATES

Retrievals were performed using microwindows in both the A-band and B-band. However, retrieving just one value for aerosol across the entire spectral region means we should restrict our spectral range for performing the retrieval to either the A-band feature or the B-band feature. Retrievals showed insignificant differences between the two. Retrievals in future work will be performed using B-band microwindows.

CALCULATING RATE CONSTANTS

Rate constants, k, reaction (2), and J, reaction (6), are calculated considering the diurnal variation in NO and N2O. Considering reactions (2) and (3) and assuming steady state NOx, expected concentrations of N2O and NO at night are given by:

\[
\frac{[N]_{2O}}{[N]_{2O}} = \frac{1}{1 - \exp(-2[R(\lambda) - J(\lambda)] \cdot t)} \cdot \left(1 + \exp(-2[R(\lambda) - J(\lambda)] \cdot t)\right)
\]

Concentrations of N2O during the day decay exponentially, mainly through photolysis:

\[
\frac{[N]_{2O}}{[N]_{2O}} = \exp(-J(\lambda) \cdot t)
\]

MIPAS sits in a sun-synchronous orbit. So to obtain variation in time since sunset, data is gathered over a 6 month period from June-December 2003. Time since sunset is calculated to consider effects of elevation, which can be significant in the stratosphere. To allow for the determination of the residual N2O at sunset, an iterative calculation was performed to determine k, J, [NO]0, and residual [N2O]0 using retrieval values of NO, NO2 and O3. The residual is found to be negligible in most cases.

CONCLUSIONS AND FUTURE WORK

Improvements to the N2O retrieval have allowed us to perform some indirect measurements of NO and estimate rate constants associated with NO chemistry in the stratosphere.

NO estimates show first order agreement with IMK-IAA NO profiles although discrepancies need to be investigated. The seasonal and latitudinal agreement should also be examined.

Estimates of the time constant, k, in the mid-stratosphere are often in agreement with laboratory values. However, the source of the high bias in NO needs to be determined. NOx data is currently being reprocessed using new B-band microwindows. An improved estimation of J, accounting for solar zenith angle dependence is under investigation.

References

1. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modelling. JPL, publication 97-4