

THE BLISS MEASUREMENTS OF NO₂: SOME NEW INSIGHTS

D.J. Lary and J.A. Pyle

Department of Chemistry, Cambridge University, UK.

C.R. Webster and R.D. May

Jet Propulsion Laboratory, California Institute of Technology

Abstract - The diurnal variation of NO₂ measured near 30 km by the BLISS in-situ laser spectrometer is compared with calculations from a photochemical model that includes a detailed description of multiple scattering.

Introduction

In a recent paper, the stratospheric chemistry of NO₂ was studied by combining high resolution tunable diode laser measurements from the balloon-borne laser in-situ spectrometer (BLISS) with a numerical model [Webster et al., 1990]. When the model was constrained with the measured O₃ and temperature, the main features of the observed diurnal variation of NO₂ were well reproduced by the model. In general, the study constituted a very successful confirmation of our present understanding of this subset of stratospheric chemistry. However, there were some differences in detail between the model and observations (Figure 1). In particular, the one daytime measurement of NO₂ could not be reproduced unless an unrealistically large value of the ground albedo was used, and there was a very rapid, but very brief, decline in the measured NO₂ immediately after the major sunset increase which the model did not reproduce. Finally some minor differences between the modelled and observed nighttime decays were evident with the model slightly overestimating the values immediately prior to dawn.

This study reconsiders the detailed aspects of the model data intercomparison. We have used a numerical model with similar chemical kinetics but a much more sophisticated treatment of scattering than that used in the earlier study. The radiative transfer model is a new implementation of the scheme described by Meier et al. (1982). It has been extended after Anderson (1983) to describe correctly the radiation field for solar zenith angles greater than 75°. The radiation into any volume element of the model atmosphere has four contributions: The direct solar flux, the diffuse flux incident from all directions, the ground reflection of the direct solar flux and the ground reflection of the diffuse flux. In this paper clear sky conditions have been assumed. Excellent validation of the scheme against various data sets has been achieved [Lary and Pyle, in press, 1991a,b].

Copyright 1991 by the American Geophysical Union.

Paper number 91GL02732
0094-8534/91/91GL-02732\$03.00

Results

In addition to several other species Webster et al. (1990); May and Webster (1989), made simultaneous in-situ measurements of NO₂, O₃, temperature, and pressure from the balloon based BLISS instrument launched at Palestine, Texas (32°N, 96°W), on 13 September, 1988. These measurements allowed a critical test of the photochemical model to be made, with very small differences between theory and data as discussed above.

This new study has reproduced some of the finer BLISS measurement details (Figure 2) with a model/measurement agreement of < 10%, which is comparable to the measurement uncertainties of 8% for sunset and nighttime NO₂, and 10% for the daytime NO₂ measurement. The model used to produce Figure 2 has a ground albedo of 0.25, a constant temperature of 233 K, a constant ozone concentration of 8.5 ppmv, and a total reactive nitrogen content of 15.24 ppbv. The model pressure is kept at 11.0 mb, except for one hour after sunset, when it is raised to 11.6 mb in accordance with the observations of Webster et al. (1990).

Firstly, as pointed out by Webster et al. (1990), the single day time measurement of NO₂ could only be explained using their scattering scheme based on Kurzeja (1976), if a ground albedo of 0.5 was used. This is an unrealistic value for desert like conditions. When the detailed treatment of multiple scattering is used at all wavelengths, then the single day time measurement of NO₂ can be explained to within the measurement uncertainty by a ground albedo of 0.25 (Figure 2).

Secondly, the peak in NO₂ concentration which occurred just after sunset can be reproduced if the slight, but brief, descent of the balloon which occurred then is included in the model. This descent was accompanied by an increase in the pressure, and hence, in the total number density. Note that in their model calculations Webster et al. (1990) used a constant value for the total number density of 3.6×10^{17} molecules cm⁻³. The observed peak would be less obvious if the concentration of NO₂ was expressed as a volume mixing ratio.

Finally, in the Webster et al. (1990) study the modelled NO₂ prior to sunrise slightly overestimated the measured values, although the measured and modelled nighttime decay certainly agreed within the experimental error. Webster et al. (1990), discussed the sensitivity of the decay to temperature. By using a temperature of 233 K, instead of 231 K as used in the earlier study, even better agreement is found, especially immediately before dawn.

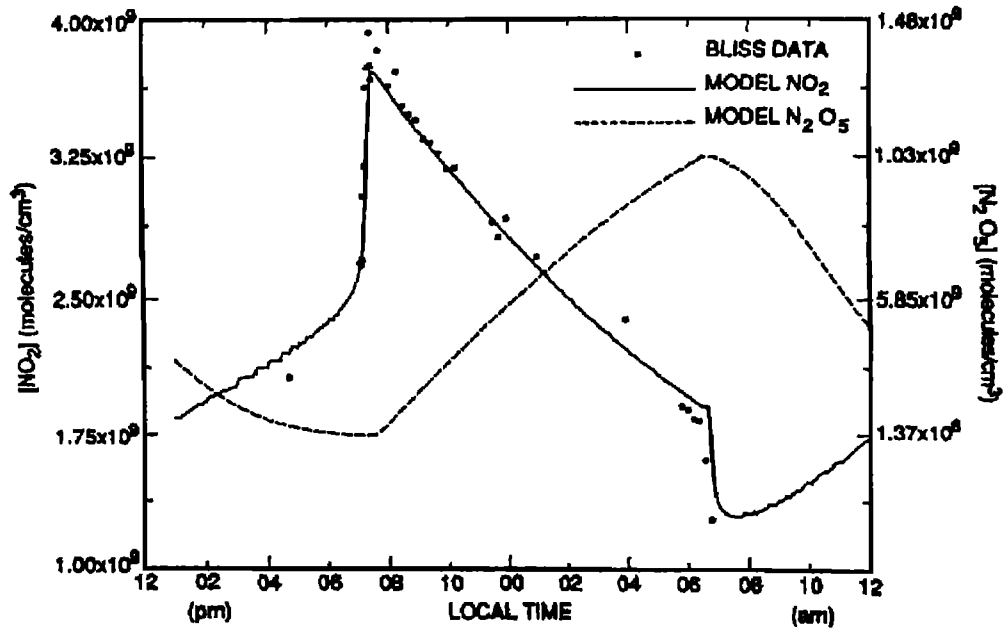


Fig. 1. A comparison of the diurnal variation of NO₂ close to 11 mb measured by BLISS (squares) and the model of Webster et al. (1990). The measurement data is tabulated in Webster et al. (1990).

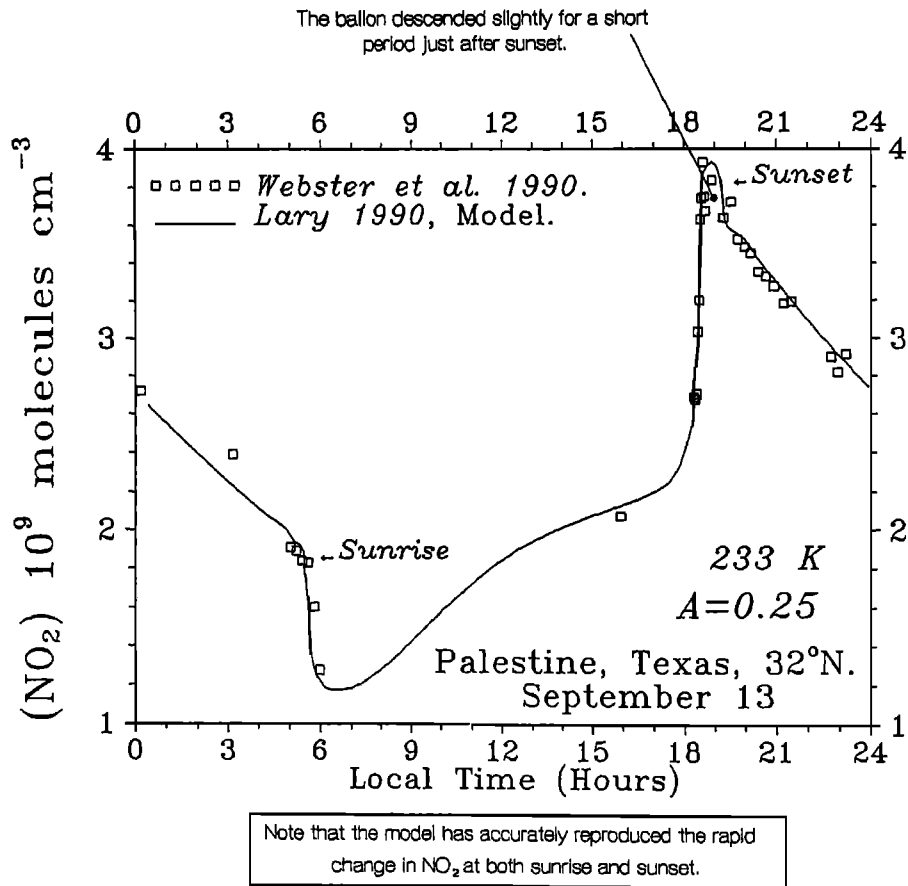


Fig. 2. A comparison of the diurnal variation of NO₂ close to 11 mb measured by Webster et al. (1990) (squares) and the model used in this study (line).

Conclusions

The data presented by Webster et al. (1990), have been compared with a new numerical model including an improved radiative transfer scheme. We now find even better agreement between the data and the model, both at sunset and during the day. We confirm the conclusions of the earlier study that the high resolution in-situ measurements of NO₂ have enabled a very successful confirmation of our understanding of the diurnal chemistry of NO₂.

Acknowledgements. D. Lary thanks SERC for a studentship and R. Toumi for many helpful discussions.

References

- Anderson, D.E., The troposphere to stratosphere radiation field at twilight: A spherical model, Planet. Space Sci., **31**, 1517-1523, 1983.
- Lary, D.J., Photochemical studies with a three-dimensional model of the atmosphere, PhD Thesis, University of Cambridge, Cambridge, England. 1991.
- Lary, D.J., and J.A. Pyle, Diffuse radiation, twilight, and photochemistry - I, Journal of Atmospheric Chemistry, In Press, 1991a.
- Lary, D.J., and J.A. Pyle, Diffuse radiation, twilight, and photochemistry - II, Journal of Atmospheric Chemistry, In Press, 1991b.
- Kurzeja, R., Effects of diurnal variations and scattering on ozone in the stratosphere for present day and predicted future chlorine concentrations, J. Atmos. Sci., **34**, 1120-1129, 1976.
- May, R.D, and C.R. Webster, In-situ stratospheric measurement of HNO₃ and HCl near 30 km using the balloon-borne laser in-situ sensor tunable diode laser spectrometer, J. Geophys. Res., **94**, 16343-16350, 1989.
- Meier, R.R., D.E. Anderson, and M. Nicolet, The radiation field in the troposphere and stratosphere from 240 to 1000 nm: General analysis, Planet. Space Sci., **30**, 923-933, 1982.
- Webster, C.R., R.D. May, R. Toumi, and J.A. Pyle, Active nitrogen partitioning and the nighttime formation of N₂O₅ in the stratosphere: Simultaneous in-situ measurements of NO, NO₂, HNO₃, O₃ and N₂O using the BLISS diode laser spectrometer, J. Geophys. Res., **95**, 13851-13866, 1990.

D.J. Lary and J.A. Pyle, Department of Chemistry, Cambridge University, Lensfield Road, Cambridge, CB2 1EW, UK.

R.D. May and C.R. Webster, Jet Propulsion Laboratory, California Institute of Technology, USA.

(Received August 14, 1991;
accepted September 28, 1991)