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MEASUREMENTS OF STRATOSPHERIC NO, NO_2 AND N_2O_5 BY ISAMS: PRELIMINARY OBSERVATIONS AND DATA VALIDATION

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ABSTRACT

The Improved Stratospheric and Mesospheric Sounder (ISAMS) is a multichannel radiometer and forms part of the science payload of the Upper Atmosphere Research Satellite (UARS). ISAMS measures infrared emissions from the Earth's atmosphere in several wavelength bands. Three such bands include emission from nitric oxide, nitrogen dioxide and dinitrogen pentoxide. In this paper we briefly discuss how the ISAMS instrument measures NO, NO_2 and N_2O_5, present preliminary data from these channels and describe preliminary validation work.

1. INTRODUCTION

Catalytic reactions involving NO and NO_2 are responsible for controlling the abundance of O_3 throughout much of the stratosphere. In order to understand the behaviour of stratospheric O_3, it is essential that the processes which affect NO and NO_2 are understood. A vital contribution to this understanding are global measurements of the abundance of NO, NO_2 and other members of the odd nitrogen (NO_x) family.

Global measurements of stratospheric NO_2 at specific times of day have been made by previous satellite instruments, i.e. the Limb Infrared Monitor of the Stratosphere on Nimbus 7 (Russell et al., 1984) and the visible spectrometer on the Solar Mesosphere Explorer (Mount et al., 1984). SAGE I and II have also accumulated global NO_2 data by near-UV solar occultation measurements from space (Chu and McCormick, 1986; Cunnold et al., 1991). In addition, vertical profiles of NO, NO_2 and N_2O_5 have been obtained at a restricted set of latitudes from IR solar occultation measurements by the ATMOS (Russell et al., 1988) and Grille (Laurent et al., 1985) spectrometers on board the space-shuttle . However, most information concerning the diurnal variation and vertical profiles of these molecules has come from balloon *in situ* and remote sensing measurements at northern mid-latitudes (Pommereau, 1982; Roscoe, 1982; Roscoe et al., 1986; Kondo et al., 1988; Webster et al., 1990 and Abbas et al., 1991).

2. ISAMS MEASUREMENTS

The first height-resolved, global measurements of NO and N_2O_5 in the stratosphere are currently being made by the Improved Stratospheric and Mesospheric Sounder (ISAMS), along with the Cryogenic Limb Array Etalon Spectrometer (CLAES), on the Upper Atmosphere Research Satellite (UARS). These, together with simultaneous measurements of NO_2, HNO_3, N_2O and other molecules, will allow the global budget and partitioning of stratospheric NO_x to be investigated more thoroughly than has been possible hitherto. The data will also be used to investigate the effects on the stratosphere of major volcanic eruptions which occurred during 1991, notably Mt.Pinatubo, specifically by examining the effect of sulphate aerosol upon the global abundance and partitioning of NO_x.

ISAMS measures IR emission from the atmosphere using $\approx 100 cm^{-1}$ wide optical filters matched to the fundamental vibration-rotation bands of NO, NO_2 and N_2O_5 at 5.3μm, 6.2μm and 8.1μm respectively. Atmospheric emission from within these filters is modulated at 1 kHz by 100% mechanical chopping and signals synchronously detected at this frequency are referred to as wide-band (WB) measurements.

For NO and NO_2, a gas-correlation technique is used in addition to the optical filters. Cells containing NO and NO_2 are included in the optical paths of these channels and their pressures cycled at $\approx$35Hz by a piston driven at resonance. Signals synchronously detected in the 35 Hz side-bands to chopper frequency are referred to as pressure modulated (PM) measurements. Simultaneous PM and WB measurements should allow retrievals of NO and NO_2 even in the presence of substantial aerosol and interfering gas emissions (Roscoe et al., 1986).

ISAMS views the atmospheric limb at right angles to the UARS velocity vector and measurements are made every two seconds. The tangent-height for each measure-

ment is determined by the position of a scanning mirror which is programmed to sample tangent-heights between 10km and 80km in 2.5km steps. NO and NO_2 signals are recorded at each mirror step; N_2O_5 signals are recorded less frequently because this filter is multiplexed with those at other wavelengths by a four-position filter wheel.

Validation of data from the ISAMS NO_x channels is still at an early stage, so accuracies have yet to be determined, however, the precision is very high. For example, the signal to noise ratio in the NO_2 PM channel is sufficient for inversion of individual limb scans. The instantaneous field of view of ISAMS is 2.5km high by 8km wide at the limb, and vertical profiles of NO_2 mixing ratio are generated every 32 seconds, or approximately 200km along the sub-tangent point track. The intrinsic vertical resolution of the measurements can be assessed by the sharpness of the averaging kernels associated with radiance inversion. Averaging kernels for the NO_2 PM channel shown in figure 1 indicate that good height resolution can be achieved throughout the stratosphere.

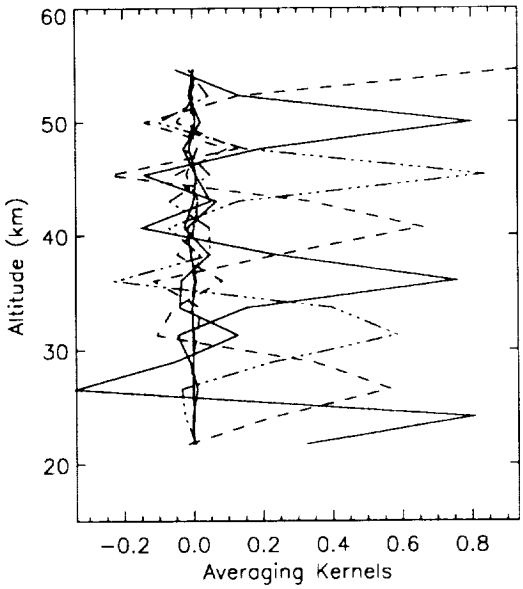

Figure 1 Averaging kernels for the NO_2 PM channel

3. DATA VALIDATION

A programme to validate ISAMS measurements of NO, NO_2 and N_2O_5 is in progress. This includes critical examination of the radiometric calibration and the resultant calibrated radiances as well as in-depth examination of instrumental parameters concerning the gas-correlation cells.

Calibration includes characterising scan-dependent stray radiation and the radiometric "zero". Accurate determination of radiometric zero in the NO PM channel is particularly important because radiances from the stratosphere are small, and small changes are important scientifically. Obtaining a good zero is, however, complicated by emission from NO in the thermosphere (see Ballard et al., this symposium).

For gas-correlation measurements, detailed knowledge of gas cell conditions is also essential, and these are partially controlled by a silicalite molecular sieve to which the cell is connected. The mean pressure in each cell is a few millibars, and can be changed by varying the temperature of the sieve by ground command. The gas cells were filled some 2 years before UARS was launched and, at that time, mean gas pressure, piston oscillation frequency and sieve temperature were carefully characterised. In orbit, the mean pressure in a given modulator cell can be derived from the resonant frequency of the piston and also from the sieve temperature, by reference to the pre-launch characterisation.

The composition of the NO and NO_2 cells is believed to have changed somewhat since filling due to chemical reactions occurring on the sieves. In the NO cell, total pressure at nominal sieve temperature has fallen since launch by $\approx$10%, which is believed to be due to interconversion of NO into N_2O and N_2O_3. In the NO_2 cell, it is estimated that $\geq$75% of gas is now NO.

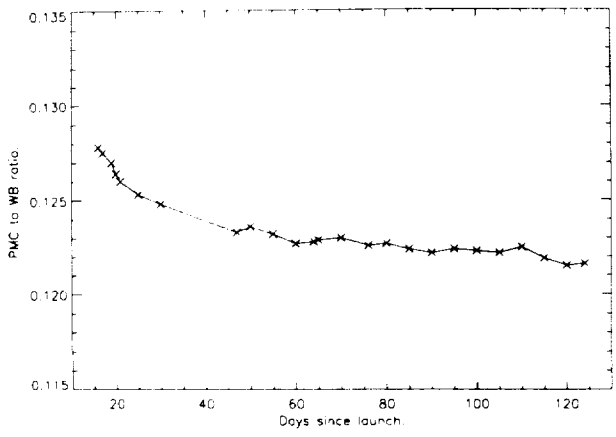

Figure 2 Ratio of PM/WB signals in the NO_2 channel when viewing the internal calibration black-body.

More accurate estimates of gas partial pressures in the two cells will be obtained from (i) measurements of resonant frequency (ie total pressure) vs sieve temperature performed recently in orbit and (ii) analysis of signals from the calibration black-body. The first exploits the unique relationship between equilibrium pressure of each molecule

and sieve temperature, which is determined by "binding energy" and other physical properties. The second exploits the unique relationship between the partial pressure of absorbing gas and the ratio of black-body signals in the WB and PM channels. Comparison of measured and calculated ratios is currently limited by knowledge of both NO_2 spectroscopy, particularly self- and NO-broadened linewidths, and the detailed pressure and temperature cycles. However, the measured ratio itself serves as an indicator of how cell composition has changed with time and figure 2 shows that only small changes have occurred since activation of ISAMS in orbit.

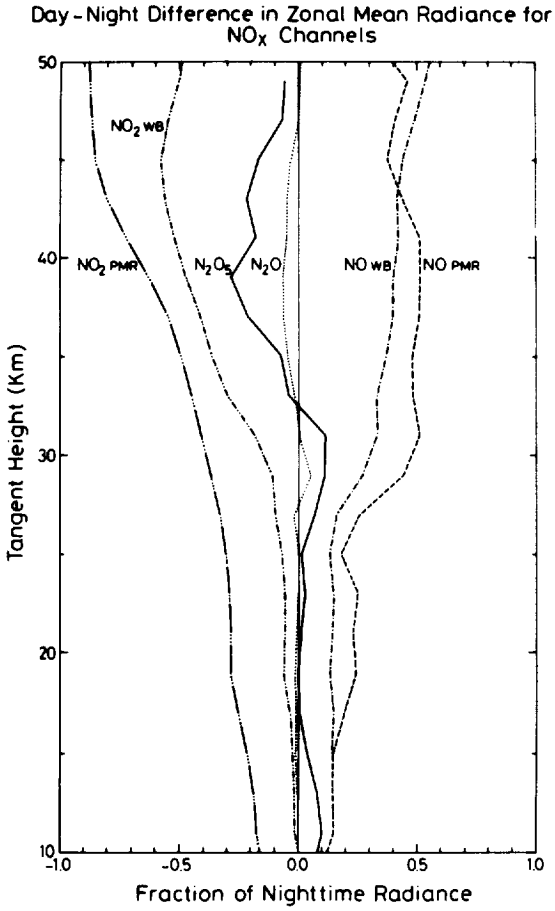

Figure 3 Day-night difference in zonal mean radiance from the NO, NO_2 and N_2O_5 channels and the N_2O WB channel for latitudes between 10°S and 50°S on 4th November 1991.

Another important aspect of the validation activity is examination of the flight data for expected atmospheric signatures. Three such signatures are reported here: (i) the day-night difference in zonally-averaged radiance; (ii) the step-wise change in NO_2 on crossing the terminator at high latitude and (iii) the steep latitudinal gradient in NO_2 at northern mid-latitude, known as the "Noxon cliff" (Noxon, 1979).

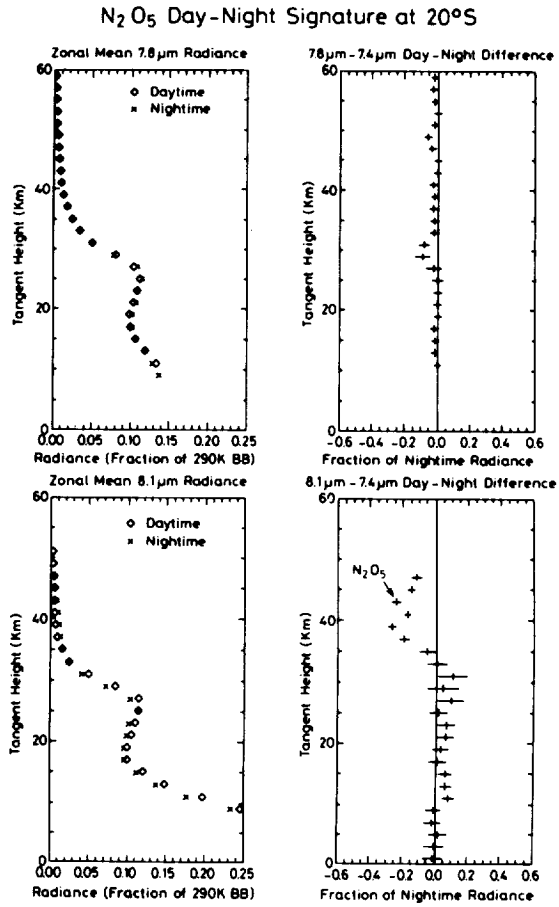

Figure 4 Zonal mean radiance profiles in the 7.8μm (N_2O) and 8.1μm (N_2O_5) channels and corresponding day-night difference profiles referenced to that in the 7.4μm (CH_4) channel.

Signals from the NO_x channels are all expected to show substantial diurnal variation induced by photochemistry, and this is evident in figure 3 where day-night differences in radiance for all NO_x channels, and also the 7.8μm (N_2O) WB channel, are plotted vs tangent-height. The data are zonal mean averages for latitudes between 10°S and 50°S for 4th November 1991. The plot indicates that ISAMS measurements are in qualitative agreement with theory: NO_2 and N_2O_5 nighttime radiances are larger than daytime values and NO daytime radiances are larger than nighttime values. Any such differences in the 7.8μm (N_2O)

or 7.4μm (CH_4) WB channels must be indicative of temperature and/or sampling effects because neither CH_4 nor N_2O exhibit any diurnal variation due to photochemistry. Effects due to temperature and sampling should be very similar in the 8.1μm (N_2O_5) channel because emission is predominantly from the same constituents and is very close in wavelength.

The significantly larger day-night difference at 8.1μm therefore gives confidence that ISAMS is detecting the diurnal signature of N_2O_5 in the upper stratosphere.

This conclusion is further supported by figure 4 which shows, in the left upper and left lower panels respectively, zonal mean radiance profiles from the 7.8μm (N_2O) and 8.1μm (N_2O_5) WB channels. Day-night difference profiles were generated from these data and then subtracted from a day-night difference profile from the 7.4μm (CH_4) WB channel. The subtracted profiles are shown in the right hand panels of figure 4. In the case of $(\text{day-night})_{7.8\mu m}$ - $(\text{day-night})_{7.4\mu m}$, most values are close to zero, as would be expected, indicating that temperature and sampling effects have been largely removed. In the case of $(\text{day-night})_{8.1\mu m}$ - $(\text{day-night})_{7.4\mu m}$, values around 40km differ significantly from zero, indicating a diurnal signature which is unlikely to be due to temperature or sampling effects.

Radiance profiles from the NO_2 PM channel have also been examined as the tangent-point crosses the terminator at high, northern latitudes. Figure 5 shows the signal from NO_2 as a function of height, which is seen to increase as the tangent-point moves from daylight into darkness, in qualitative accord with theory.

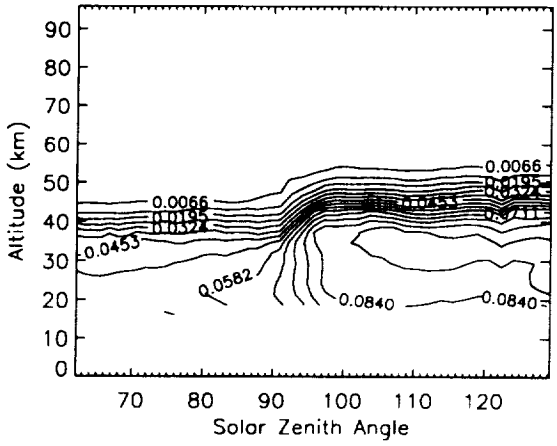

Figure 5 Terminator crossing observed in the NO_2 PM channel

The geographical distribution of retrieved NO_2 has also been examined. Figure 6 shows the distribution of NO_2 (relative amounts) for 9/1/92 at 30km altitude. The steep reduction in NO_2 at northern mid-latitudes and longitudes between 0° and 90°W is strongly suggestive of the so-called "Noxon cliff".

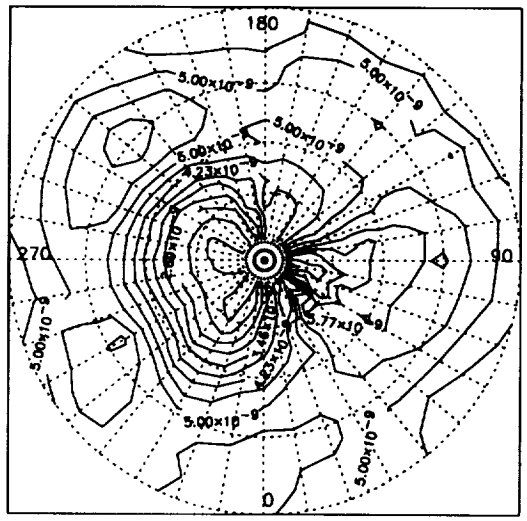

Figure 6 Retrieved NO_2 (relative amounts) at 30km on 9th January 1992

4. FUTURE WORK

A substantial amount of work still remains before validated nitrogen oxides data will be available from ISAMS. For NO, this includes provision of a source function for $1 \rightarrow 0$ emission throughout the stratosphere, mesosphere and lower thermosphere and accurate determination of cell composition. Refinement of the way in which the PM space-view signal is derived may also be necessary. For NO_2, a lot more work is needed to obtain the best estimate of gas composition in the modulator cell, including high resolution spectroscopy of NO_2 and measurements of pressure and temperature cycles in a flight-spare modulator. For N_2O_5, despite careful choice of optical filter, other atmospheric constituents, notably CH_4, N_2O and aerosol, contribute substantial radiance. Reliable N_2O_5 retrievals must therefore await accurate, validated retrievals of these constituents from other ISAMS channels (eg. Lambert et al., this symposium).

Once this work has been accomplished, a detailed intercomparison of retrieved profiles will be undertaken as part of the UARS validation campaign. This will include measurements by other UARS sensors, the ATLAS mission and ground-based, aircraft and balloon instruments.

REFERENCES

Abbas, M. M., V. G. Kunde, J. C. Brasunas, J. R. Herman, and S. T. Massie, 1991: Nighttime reactive nitrogen measurements from stratospheric infrared thermal emission observations. *J. Geophys. Res.*, 96, 10885.

Chu, W. P. and M. P. McCormick, 1986: SAGE observations of stratospheric nitrogen dioxide. *J. Geophys. Res.*, 91, 5465.

Cunnold, D. M., J. M. Zawodny, W. P. Chu, J. P. Pommereau, F. Goutail, J. Lenoble, M. P. McCormick, R. E. Veiga, D. Murcray, N. Iwagami, K. Shibasaki, P. C. Simon, and W. Peetermans, 1991: Validation of SAGE II NO_2 measurements. *J. Geophys. Res.*, 96, 12913.

Kondo, Y., W. A. Mathews, P. Aimedieu, and D. E. Robbins, 1988: Diurnal variation of nitric oxide at 32km: measurement and interpretation. *J. Geophys. Res.*, 93, 2451.

Laurent, J., M. Lemaitre, J. Besson, A. Girard, C. Lippens, C. Muller, J. Vercheval, and M. Ackerman, 1985: Middle atmosphere NO and NO_2. *Nature*, 315, 126.

Mount, G. M., D. W. Rusch, J. F. Noxon, J. M. Zawodny, and C. A. Barth, 1984: Measurements of stratospheric NO_2 from the Solar Mesospere Explorer Satellite: 1. An overview of results. *J. Geophys. Res.*, 80, 1327.

Noxon, J. F., 1979: Stratospheric NO2 - 2. Global Behaviour. *J. Geophys. Res.*, 84, 5067.

Pommereau, J. P., 1982: Observation of NO_2 diurnal variation in the stratosphere. *Geophys. Res. Lett.*, 9, 850.

Roscoe, H. K., 1982: Tentative observation of stratospheric N_2O_5. *Geophys. Res. Lett.*, 9, 901.

Roscoe, H. K., B. J. Kerridge, L. J. Gray, R. J. Wells, and J. A. Pyle, 1986: Simultaneous measurements of stratospheric NO and NO_2 and their comparison with model predictions. *J. Geophys. Res.* 91, 5405.

Russell III, J. M., J. C. Gille, E. E. Remsberg, L. L. Gordley, P. L. Bailey, S. R. Drayson, H. Fischer, A. Gerard, J. E. Harries, and W. J. Evans, 1984: Validation of nitrogen dioxide results measured by the Limb Infrared Monitor of the Stratosphere (LIMS) experiment on Nimbus 7. *J. Geophys. Res.*, 89, 5099.

Russell III, J. M., C. B. Farmer, C. P. Rinsland, R. Zander, L. Froidevaux, G. C. Toon, B. Gao, J. Shaw, and M. Gunso, 1988: Measurements of odd nitrogen compounds in the stratosphere by the ATMOS experiment on Spacelab 3. *J. Geophys. Res.*, 93, 1718.

Webster, C. R., and R. D. May, 1990: Active nitrogen partitioning and the nighttime formation of N_2O_5 in the stratosphere: simultaneous *in situ* measurements of NO, NO_2, HNO_3, O_3 and N_2O_5 using the BLISS diode laser spectrometer. *J. Geophys. Res.*, 95, 13851.