MEASUREMENTS OF STRATOSPHERIC NO, NO₂ AND N₂O₅ 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, NO₂ and N₂O₅, present preliminary data from these channels and describe preliminary validation work.

1. INTRODUCTION

Catalytic reactions involving NO and NO₂ are responsible for controlling the abundance of O₃ throughout much of the stratosphere. In order to understand the behaviour of stratospheric O₃, it is essential that the processes which affect NO and NO₂ are understood. A vital contribution to this understanding are global measurements of the abundance of NO, NO₂ and other members of the odd nitrogen (NOₓ) family.

Global measurements of stratospheric NO₂ 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 NO₂ data by near-UV solar occultation measurements from space (Chu and McCormick, 1986; Cunnold et al., 1991). In addition, vertical profiles of NO, NO₂ and N₂O₅ 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 N₂O₅ 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 NO₂, HNO₃, N₂O and other molecules, will allow the global budget and partitioning of stratospheric NOₓ 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 NOₓ.

ISAMS measures IR emission from the atmosphere using 100 cm⁻¹ wide optical filters matched to the fundamental vibration-rotation bands of NO, NO₂ and N₂O₅ 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 NO₂, a gas-correlation technique is used in addition to the optical filters. Cells containing NO and NO₂ are included in the optical paths of these channels and their pressures cycled at ~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 NO₂ 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 NO₂ signals are recorded at each mirror step; N₂O₅ 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 NOx 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 NO₂ 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 NO₂ 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 NO₂ PM channel shown in figure 1 indicate that good height resolution can be achieved throughout the stratosphere.

![Figure 1: Averaging kernels for the NO₂ PM channel](image)

3. DATA VALIDATION

A programme to validate ISAMS measurements of NO, NO₂ and N₂O₅ 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 NO₂ 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 ≈10%, which is believed to be due to interconversion of NO into N₂O and N₂O₅. In the NO₂ cell, it is estimated that ≥75% of gas is now NO.

![Figure 2: Ratio of PM/WB signals in the NO₂ channel](image)
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 NO₂ 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, NO₂ and N₂O₃ channels and the N₂O 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 NO₂ on crossing the terminator at high latitude and (iii) the steep latitudinal gradient in NO₂ at northern mid-latitude, known as the "Noxon cliff" (Noxon, 1979).

Figure 4 Zonal mean radiance profiles in the 7.8μm (N₂O₃) and 8.1μm (N₂O₅) channels and corresponding day-night difference profiles referenced to that in the 7.4μm (CH₄) channel.

Signals from the NO₂ 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 NO₂ channels, and also the 7.8μm (N₂O₃) 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: NO₂ and N₂O₅ nighttime radiances are larger than daytime values and NO daytime radiances are larger than nighttime values. Any such differences in the 7.8μm (N₂O)
or 7.4 μm (CH₄) WB channels must be indicative of temperature and/or sampling effects because neither CH₄ nor N₂O exhibit any diurnal variation due to photochemistry. Effects due to temperature and sampling should be very similar in the 8.1 μm (N₂O) channel because emission is predominantly from the same constituents and is very close in wavelength.

The significantly larger day-night difference at 8.1 μm therefore gives confidence that ISAMS is detecting the diurnal signature of N₂O 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 7.8 μm (N₂O) and 8.1 μm (N₂O₃) WB channels. Day-night difference profiles were generated from these data and then subtracted from a day-night difference profile from the 7.4 μm (CH₄) WB channel. The subtracted profiles are shown in the right hand panels of figure 4. In the case of (day-night)₇.₈μm - (day-night)₇.₄μm, most values are close to zero, as would be expected, indicating that temperature and sampling effects have been largely removed. In the case of (day-night)₈.₁μm - (day-night)₇.₄μm, values around 40 km differ significantly from zero, indicating a diurnal signature which is unlikely to be due to temperature or sampling effects.

Radiance profiles from the NO₂ PM channel have also been examined as the tangent-point crosses the terminator at high, northern latitudes. Figure 5 shows the signal from NO₂ as a function of height, which is seen to increase as the tangent-point moves from daylight into darkness, in qualitative accord with theory.

The geographical distribution of retrieved NO₂ has also been examined. Figure 6 shows the distribution of NO₂ (relative amounts) for 9/1/92 at 30 km altitude. The steep reduction in NO₂ at northern mid-latitudes and longitudes between 0° and 90° W is strongly suggestive of the so-called "noxon cliff".

Figure 5 Terminator crossing observed in the NO₂ PM channel

Figure 6 Retrieved NO₂ (relative amounts) at 30 km on 9 th 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→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 NO₂, a lot more work is needed to obtain the best estimate of gas composition in the modulator cell, including high resolution spectroscopy of NO₂ and measurements of pressure and temperature cycles in a flight-spare modulator. For N₂O₃, despite careful choice of optical filter, other atmospheric constituents, notably CH₄, N₂O and aerosol, contribute substantial radiance. Reliable N₂O₃ 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


