MIPAS measurement of sulphur hexafluoride (SF_6)

A. B. Burgess, R. G. Grainger, A. Dudhia, and V. H. Payne
Atmospheric, Oceanic and Planetary Physics, University of Oxford, Oxford, UK

V. L. Jay
Rutherford Appleton Laboratory, Chilton, Didcot, UK

Received 24 November 2003; revised 30 December 2003; accepted 3 February 2004; published 9 March 2004.

[1] The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a polar orbiting high resolution mid-infrared emission stratospheric limb sounder with a nominal vertical resolution of 3 km. Work to extend the list of interesting, routinely retrieved species led to the examination of SF_6, a potent greenhouse gas and a useful tracer species. We demonstrate the feasibility of profile retrievals in the range 6–30 km based on single scans. Additionally, we investigate latitudinal variation using coaddition to improve signal-to-noise. A mean mid-latitude profile shows tropospheric (4.32 ± 0.03 pptv, 6–12 km) and stratospheric (3.50 ± 0.03 pptv, 21–30 km) regimes, in September 2002, similar to accepted values. The global mean contains an inter-hemispheric variability of the order of 0.3 pptv in the lower stratosphere, in line with age of air. Finally, the continuation of acknowledged global trends in atmospheric concentration, is estimated at +0.28 pptv yr^{-1} (6.5 ± 1.3% yr^{-1}). *INDEX TERMS:* 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0394 Atmospheric Composition and Structure: Instruments and techniques; 3360 Meteorology and Atmospheric Dynamics: Remote sensing; 3394 Meteorology and Atmospheric Dynamics: Instruments and techniques. **Citation:** Burgess, A. B., R. G. Grainger, A. Dudhia, V. H. Payne, and V. L. Jay (2004), MIPAS measurement of sulphur hexafluoride (SF_6), *Geophys. Res. Lett.*, *31*, L05112, doi:10.1029/2003GL019143.

1. Introduction

[2] Sulphur hexafluoride (SF_6) is one of the most efficient greenhouse gases: it is three times stronger as a 'greenhouse gas' than an equivalent volume mixing ratio (VMR) of CFC-11 [*Ko et al.*, 1993] and a thousand times that of CO_2. The contribution of SF_6 to radiative forcing is small because its current atmospheric concentration is less than five parts per trillion by volume (pptv) [*Maiss et al.*, 1996; *Maiss and Levin*, 1994; *Zander et al.*, 1991; *Rinsland et al.*, 2003]. The sources of SF_6 are almost entirely anthropogenic [*Ko et al.*, 1993] although traces may originate naturally from fluoritic rocks [*Harnisch and Eisenhauer*, 1998]. As the atmospheric lifetime of SF_6 is of the order of several thousand years [*Patra et al.*, 1997] there is the potential for the gas to slowly accumulate in the atmosphere and to become a significant contributor to radiative forcing.

[3] There is evidence that the atmospheric concentration of SF_6 is increasing by about 7–8% per year [*Maiss et al.*, 1996; *Rinsland et al.*, 1993]. However, it has been suggested that the rate of increase in emission, if not production, has slowed in the past few years [*Maiss and Brenninkmeijer*, 1998; *Connell et al.*, 2000].

[4] In this paper, we describe the retrieval of SF_6 profiles from measurements made by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS). We validate the results against internal and external data and add to the knowledge of SF_6 trends.

2. MIPAS Measurement of SF_6

[5] MIPAS was launched as part of Europe's environmental monitoring satellite, Envisat, aboard an Ariane-5 rocket on 1st March 2002. Envisat was injected into a polar orbit at an altitude of about 800 km and has an orbital period of about 100 minutes [*European Space Agency* (*ESA*), 2000a, 2000b]. MIPAS is an actively cooled atmospheric thermal emission limb sounder, working in the mid-infrared with a field-of-view that is approximately 3 × 30 × 300 km. MIPAS obtains high resolution spectra (0.025 cm^{-1}) that cover the range 685–2410 cm^{-1} (14.6–4.15 μm). A complete limb scan sequence consists of 17 spectra with tangent points at 68 km, 60 km, 52 km, 47 km, 42 km and downward to 6 km in 3 km steps.

2.1. Pre-Processing

[6] A problem in limb profile retrievals is contamination of the lower views with cloud. If a set of retrievals is performed over an entire orbit, it becomes obvious where significant cloud is located because poor retrieval convergence is observed. There is a strong correlation between these scans and high continuum in the spectra. One must discard contaminated spectra by choosing the point at which the damaging influence of cloud contamination on the retrieval is minimised, whilst maximising the number of low-altitude profile points retrieved.

[7] This method of cloud detection relies on the ratio between the radiance of two small regions of the spectrum, 788.20–796.25 cm^{-1} and 832.30–834.40 cm^{-1}. A threshold value of 1.8 for this ratio has been chosen after observation of a large number of measurements by previous instruments, [*Spang et al.*, 2004]. All ratios falling below the value are flagged as cloudy. The conservative threshold of 1.8 does not take into account the continuous gradient of cloud optical thicknesses, but we expect very few cloudy sweeps to remain in our analysis.

2.2. Retrieval

[8] SF_6 is a highly symmetric octagonal molecule, point group O_h. Its main infrared vibrational-rotational transitions

0094-8276/04/2003GL019143$05.00

are centred around a single ν_3 Q branch at 947.9 cm^{-1}, with band limits 915–960 cm^{-1} [*Rinsland et al.*, 1992; *Varanasi et al.*, 1992].

[9] Figure 1 shows the SF_6 contribution to the limb radiance for the lower stratosphere. The SF_6 signal exceeds the MIPAS noise-equivalent spectral radiance (NESR) between about 944 and 951 cm^{-1}. The coverage of the six selected microwindows is also shown, along with their altitude sensitivity.

[10] The retrievals of SF_6 profiles from MIPAS data has been achieved using the Oxford Processor To Invert MIPAS Observations (OPTIMO) based on work by *Jay* [2000]. OPTIMO uses the optimal estimation method [*Rodgers*, 2000] to find the most probable solution consistent with both the measurements and the a priori knowledge. Pressure-temperature then water vapour were sequentially retrieved; all other interfering species were set to the climatological values used in the operational ESA MIPAS processor [*Ridolfi et al.*, 2000]. Rather than using all the available spectral data, it is more efficient to select microwindows, i.e., small regions of the spectrum. The selection process models the propagation of both random and systematic errors through the retrieval, providing a full error analysis over the altitude range of interest. Using microwindows offers several advantages over using a collection of isolated measurements [*Dudhia et al.*, 2002; *Ridolfi et al.*, 2000].

[11] The microwindow error analysis is shown in Figure 2. The quality of this prediction is related to the accuracy with which the individual error sources were specified. Climatological uncertainties, as used operationally, were applied for all species, with uncertainties of 1 kelvin for temperature, 2% for pressure and 60% (10 km) to 10% (25 km) for 1σ climatological water uncertainty. It indicates that the random error dominates at all altitudes, and the total error on the retrieval tends to 100 percent at around 30 km, forming a natural cutoff for retrieval attempts. Systematic error sources are defined here as correlated between measurements in a single profile. Spectroscopic errors would be constant over the year; most others would be expected to become decorrelated after a few days. The only components expected to affect the trend are those related to instrument calibration which might remain correlated for months.

2.3. Post-Processing

[12] For SF_6 there exists a small number of spectral points corresponding to a narrow feature within the measured spectral range. As a consequence, the retrievals tend to be sensitive to random error. Averaging of profiles was performed, for the whole orbit and additionally by latitude band. When calculating means of retrieved profiles, the propagation of a priori information into the final result must be taken into account. A first order level by level correction of up to 0.5% was applied. The method makes use of the retrieval error variance (σ_x^2) and the given a priori variance (σ_a^2) to calculate a set of measurement variances (σ_m^2). From this it is possible to solve for the measurement ($\hat{m}$) of the true atmosphere based on the a priori ($\hat{a}$) and retrieved ($\hat{x}$) profiles, as $\hat{m} = (\hat{x}/\sigma_x^2 - (\hat{a})/\sigma_a^2)\ (1/\sigma_x^2 - 1/\sigma_a^2)^{-1}$.

2.4. Validation

[13] Other indicators of retrieval quality and information content may be used both to assess the quality of a single profile retrieval and to assist when combining profiles to provide a mean profile where the influence of anomalous retrievals has been reduced. As always, care must be taken when manipulating intermediate data to ensure that biases are not introduced into the final result.

[14] Figure 3 shows a representative averaging kernel for a single profile retrieval from September 2002. The width is a measure of retrieval resolution. In the following results, we usually observe approximately four degrees of freedom (trace of the averaging kernel matrix).

2.5. Other MIPAS Retrievals

[15] The Institute of Atmospheric Sciences and Climate (ISAC) of the Italian National Research Council (CNR) group in Italy uses the same MIPAS data, but a different retrieval code and a single, wider microwindow approach. This allows us to investigate the relative performance of the two schemes. In the case of SF_6, both retrieval codes were applied to pre-release orbit number 2081. Discounting scans that were cloudy, the remaining SF_6 profiles compared favourably, well within the error bars for a single scan (L. Magnani, personal communication). For example, a mean tropospheric value (first 10 scans, bottom three levels) for the Oxford group was 4.19 ± 0.28 pptv and for the ISAC group, 4.17 pptv. Additional validation of the general performance of several retrieval schemes was made by blind test retrievals as part of the AMIL2DA project [*von Clarmann et al.*, 2003].

3. Results

[16] Observed vertical profiles of SF_6 from balloon [*Patra et al.*, 1997], ATMOS [*Rinsland et al.*, 1993] and recent ground-based measurements [*Rinsland et al.*, 2003], give an indication of the expected vertical distributions: these are similar to our results. There is no prior global measurement; the best previous latitudinal coverage comes from ship campaigns, such as *Geller et al.* [1997]. The ground-based measurements suffer from significantly broader weighting functions than the limb instrument offers, of the order of 10–15 km. Conversely, the limb instrument does not nominally measure below 6 km and is susceptible to cloud along its optical path.

3.1. Mean Profile

[17] The global mean profile obtained from 27 orbits is shown in Figure 4. It shows tropospheric and stratospheric regions. The decrease in VMR with altitude is attributed almost entirely to the increasing age of the air at higher altitudes, as there is no significant loss mechanism for SF_6 in the troposphere and low-to-mid stratosphere. For the global means, the number of cloud-validated northern hemispheric profiles was 836, similar to the 826 profiles for the southern hemisphere. This balance is important, as there is a known interhemispheric variation in VMR due to industrialised anthropogenic sources in the northern hemisphere and an inter-hemispheric transport time of the order of one year [*Waugh and Hall*, 2002]. It was also possible to investigate latitudinal variability and the results are overlaid on Figure 4. The features of these lines show a high sensitivity of the retrieval to temperature accuracy at 6–9 km, as the equatorial values (10N and 10S) are both lower than would be expected by any consideration of global circulation. Likewise, the polar latitudes are high to a similar degree. By 12 km it is possible to see the decrease in VMR as the line of sight enters

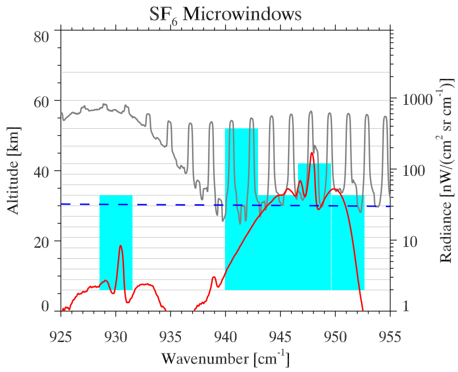

Figure 1. The region of the MIPAS spectrum containing the microwindows chosen for SF_6 retrieval (shaded regions), the instrument NESR (dashed line), SF_6 contribution (lower line) and total atmospheric radiance (upper line).

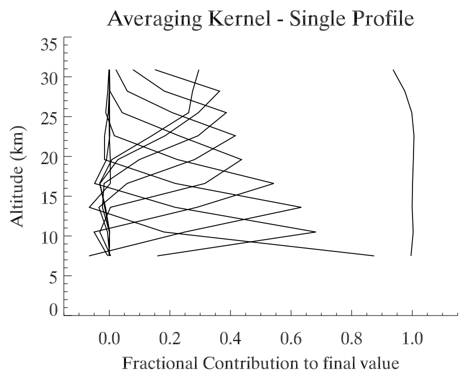

Figure 3. Representative averaging kernel for a single profile retrieval from September 2002. The width of these kernels is a measure of retrieval resolution. There are just over four degrees of freedom in this profile, indicating that of the nine levels retrieved there are four wholly independent points in the final profile. The most information-rich region is in the troposphere, due to the better signal-to-noise ratio.

the stratosphere for the mid-latitude and polar measurements, but this effect does not occur until 15–20 km over the equator, as would be expected. Finally, by 30 km the younger equatorial air shows a higher VMR than mid-latitudes which, in turn, are greater than the polar air.

3.2. Trends in VMR

[18] The trend in the atmospheric VMR of SF_6, as outlined in the introduction, has been reported in many papers over the last 20 years. Our results are shown in Figure 5, with data from other groups included. To test the sensitivity of our retrieval, we looked at measurements 13 months apart, expecting an increase of the order of 0.4 pptv corresponding to previous trend estimates in the range 7–8% yr^{-1} [*Maiss et al.*, 1996; *Rinsland et al.*, 1993, 2003]. The variation within tropospheric values for a single orbit is approximately ±0.5 pptv. Hence the consideration of multiple orbits was required to reduce this to less than 0.1 pptv to be certain of distinguishing a trend. Considering the global mean tropospheric VMR for 25 orbits taken over 5 consecutive days for both September 2002 (4.32 ± 0.03 pptv) and October 2003 (4.60 ± 0.03 pptv), the difference was 0.28 ± 0.6 pptv, giving a trend estimate of 6.5 ± 1.3% yr^{-1}. This is lower than the older estimates, but more in line with the most recent estimate of 3.34 times in 20 years by *Rinsland et al.* [2003]. It has also been suggested that the rate of increase of emission has decreased over the last 5 years due to increased environmental awareness [*Connell et al.*, 2000]. Part of our observed trend may be due to the influence of systematic errors that were changed by one of several MIPAS processor upgrades upstream of our retrieval process between September 2002 and October 2003. However, we have good reason to believe that the resultant influence on the retrievals has been small. We base this on the observed consistency of MIPAS operational products routinely analysed at Oxford

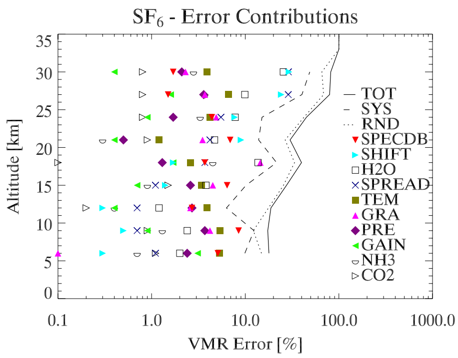

Figure 2. Plot showing random error (dotted line 'RND') to be the dominant error source in the retrieval. Subsequent significant systematic sources (total, 'SYS') are errors such as the prior retrieval of water VMR, line shape and position calibration uncertainties ('H2O', 'SPREAD' and 'SHIFT', above 20 km) and uncertainties in modelling other lines within the spectral database used in the forward model and temperature retrieval accuracy ('SPECDB', 'TEM', below 20 km). The other contributions listed are 'PRE' pressure retrieval accuracy, climatological uncertainty of 'CO2' and 'NH3', horizontal temperature gradient 'GRA' and the instrument radiometric gain error 'GAIN'.

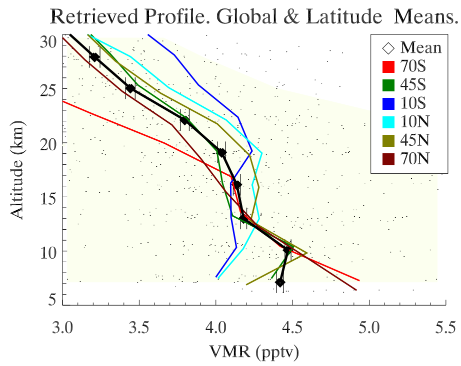

Figure 4. VMR retrievals for 27 orbits around 19th September 2002. The global mean is shown with RMS retrieval error bars. The pale shaded region represents VMRs within 100 percent of the a priori. The dots show a sample of the scatter of over 1600 retrieved profiles that comprise the mean, after cloud 'contaminated' spectra were discounted. Finally, means by latitude band are shown.

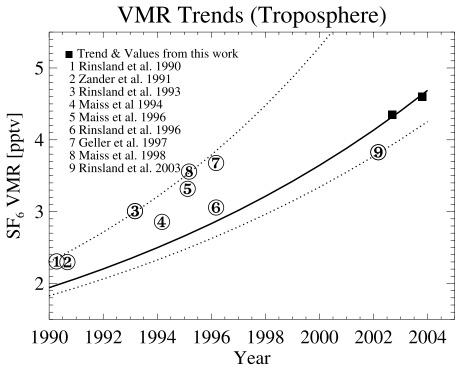

Figure 5. SF_6 trend of 6.5 ± 1.3% yr^{-1} over the current available MIPAS dataset shown as a heavy line based on mean retrieved values in September 2002 and October 2003 (squares). Similar behaviour has also been observed in the stratosphere. Dotted lines show previously reported trends from satellite (*Rinsland et al.* [1993] gives VMR 2.95 pptv increasing by 8.7% yr^{-1}) and ground-based measurements (*Rinsland et al.* [2003] gives VMR 3.77 pptv increased by 3.34 times in 20 years). Other published VMRs from the last decade are included. The circles represent the points at which the measurements were made, and the uncertainties in both trends and measurements have been omitted for clarity. It may be argued that compound percentage per annum increase is no longer a best fit to the more recent data, unlike in the early 1990s.

from July 2002. For example, the equivalent trend in retrieved methane (45N) is <1% at 12 km over the same period. A long-term systematic error in the spectral radiances would be expected to perturb the retrievals of all species. We anticipate a clearer answer within the next 12 months now the instrument calibration and validation is complete.

4. Conclusions

[19] Because of its long lifetime and strong infrared properties, better knowledge of SF_6 looks to be of increasing significance in successfully modelling the radiative processes that govern our atmosphere and climate - even though its current warming contribution is less than 1% that of CO_2, [*Ko et al.*, 1993]. SF_6 can also be used as a highly inert tracer for determining the age of stratospheric air [*Harnisch et al.*, 1996; *Waugh and Hall*, 2002].

[20] Data from MIPAS is able to provide regular information on latitudinal VMRs and on long-term trends. We have demonstrated the feasibility of profile retrievals in the range 6–30 km based on single scans, with 4–5 degrees of freedom for each profile. Averaging of multiple orbits to reduce random errors has been successful. A mean mid-latitude profile shows distinct tropospheric (4.60 ± 0.05 pptv, October 2003) and stratospheric (3.51 ± 0.05 pptv) regimes, similar to accepted values. This global mean stratospheric loading contains an inter-hemispheric variability of the order of 0.3 pptv, giving an inter-hemispheric exchange time (troposphere) of approximately one year. Finally, we have shown the continuation of acknowledged global trends in atmospheric concentration, placing our estimate at 6.5 ± 1.3% yr^{-1} (0.28 ± 0.06 pptv yr^{-1}). Future work would make use of the wealth of available MIPAS data for circulation and climate modelling.

[21] **Acknowledgments.** NERC (UK) for providing funding.

References

Connell, P. O., F. Heil, J. Henriot, G. Mauthe, H. Morrison, L. Niemeyer, M. Pittroff, R. Probst, and J. Taillebois (2000), SF_6 in the electric industry, paper presented at CIGRE 2000, Cons. Int. des. Grands Réseaux Électr., Paris.

Dudhia, A., V. Jay, and C. Rodgers (2002), Microwindow selection for high spectral resolution sounders, *Appl. Opt.*, *41*, 3665–3673.

European Space Agency (ESA) (2000a), Envisat-1: Mission and system summary, *Eur. Space Agency Sci. Tech. Rep.*, *ESA/SP-1229*, 85 pp.

European Space Agency (ESA) (2000b), Envisat MIPAS—An instrument for atmospheric chemistry and climate research, *ESA Bull.*, *101*, 14 pp.

Geller, L., J. Elkins, J. Lobert, A. Clarke, D. Hurst, J. Butler, and R. Myers (1997), Tropospheric SF_6: Observed latitudinal distribution and trends, derived emissions and interhemispheric exchange time, *Geophys. Res. Lett.*, *6*, 675–678.

Harnisch, J., and A. Eisenhauer (1998), Natural CF_4 and SF_6 on Earth, *Geophys. Res. Lett.*, *25*, 2401–2404.

Harnisch, J., R. Borchers, P. Fabian, and M. Maiss (1996), Tropospheric trends for CF_4 and C_2F_6 since 1982 derived from SF_6 dated stratospheric air, *Geophys. Res. Lett.*, *23*, 1099–1102.

Jay, V. L. (2000), Remote sounding of the atmosphere by high resolution spectroscopy, Ph.D. thesis, Univ. of Oxford, Oxford, U.K.

Ko, M., N. D. Sze, W.-C. Wang, G. Shia, A. Goldman, F. Murcary, D. Murcary, and C. Rinsland (1993), Atmospheric sulfur hexafluoride: Sources, sinks and greenhouse warming, *J. Geophys. Res.*, *98*, 10,499–10,507.

Maiss, M., and C. Brenninkmeijer (1998), Atmospheric SF_6: Trends, sources, and prospects, *Environ. Sci. Technol.*, *32*, 3077–3086.

Maiss, M., and I. Levin (1994), Global increase of SF_6 observed in the atmosphere, *Geophys. Res. Lett.*, *21*, 569–572.

Maiss, M., L. Steele, R. Francey, P. Fraser, R. L. N. Trivett, and I. Levin (1996), Sulfur hexafluoride—A powerful new atmospheric tracer, *Atmos. Environ.*, *30*, 1621–1629.

Patra, P., S. Lal, B. Subbaraya, C. H. Jackman, and P. Rajaratnam (1997), Observed vertical profile of sulfur hexafluoride (SF_6) and its atmospheric applications, *J. Geophys. Res.*, *102*, 8855–8859.

Ridolfi, M., et al. (2000), Optimized forward model and retrieval scheme for MIPAS near-real-time data processing, *Appl. Opt.*, *39*, 1323–1340.

Rinsland, C., A. Goldman, and J.-M. Flaud (1992), Infrared spectroscopic parameters of COF_2, SF_6, ClO, N_2, and O_2, *J. Quant. Spectrosc. Radiat. Transf.*, *48*, 693–699.

Rinsland, C. P., M. R. Gunson, M. C. Abrams, L. L. Lowes, R. Zander, and E. Mahieu (1993), ATMOS/ATLAS 1 measurement of sulfur hexafluoride (SF_6) in the lower stratosphere and upper troposphere, *J. Geophys. Res.*, *98*, 20,491–20,494.

Rinsland, C., A. Goldman, T. Stephen, L. Chiou, E. Mahieu, and R. Zander (2003), SF_6 ground-based infrared solar absorption measurements: Long-term trend, pollution events, and a search for SF_5CF_3 absorption, *J. Quant. Spectrosc. Radiat. Transf.*, *78*, 41–53.

Rodgers, C. (2000), *Inverse Methods for Atmospheric Sounding: Theory and Practice*, World Sci., River Edge, N. J.

Spang, R., J. Remedios, and M. Barkley (2004), Colour indices for the detection and differentiation of cloud types in infra-red limb emission spectra, *Adv. Space Res*, doi:10.1016/s0273-1177(03)00585-4, in press.

Varanasi, P., A. Gopalan, and J. Brannon (1992), Infrared absorption-coefficient data on SF_6 applicable to atmospheric remote-sensing, *J. Quant. Spectrosc. Radiat. Transf.*, *48*, 141–145.

von Clarmann, T., et al. (2003), A blind test retrieval experiment for infrared limb emission spectrometry, *J. Geophys. Res.*, *108*(D23), 4746, doi:10.1029/2003JD003835.

Waugh, D., and T. Hall (2002), Age of stratospheric air: Theory, observations, and models, *Rev. Geophys.*, *40*(4), 1010, doi:10.1029/2000RG000101.

Zander, R., C. Rinsland, and P. Demoulin (1991), Infrared spectroscopic measurements of the vertical column abundance of sulfur-hexafluoride, SF_6, from the ground, *J. Geophys. Res.*, *96*, 15,447–15,454.

A. B. Burgess, A. Dudhia, R. G. Grainger, and V. H. Payne, Atmospheric, Oceanic and Planetary Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, UK. (burgess@atm.ox.ac.uk)

V. L. Jay, Rutherford Appleton Laboratory, Chilton, Didcot OX11 0QX, UK.