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MEASUREMENT OF NIGHTTIME STRATOSPHERIC N_2O_5 FROM INFRARED EMISSION SPECTRA

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Abstract. The mixing ratio profile of N_2O_5 has been inferred from high-resolution emission spectra obtained with a balloon-borne Fourier spectrometer (SIRIS). The observations were taken for the period from midnight to predawn on September 16, 1986 at 32° N latitude. The inferred volume mixing ratio from nighttime average spectra has a peak of $\sim 1.8 \times 10^{-9}$ in the 32-35 altitude range. The inferred mixing ratio is generally less than the theoretical predictions from a 1-D model.

Introduction

The NO_x catalytic cycle, centered on the rapid interchange of NO and NO_2 free radicals, is the dominant process in the ozone chemistry in the present-day stratosphere at mid-latitudes. The destruction of O_3 by NO and NO_2 is governed by competing reactions converting the NO and NO_2 to temporary reservoir species (N_2O_5 and HNO_3). N_2O_5 is produced almost entirely at night, with about 30-50% of the total NO_x being converted to N_2O_5 . This N_2O_5 is slowly photolyzed during the daytime to NO_2 , producing the diurnal variation in NO_2 . Knowledge of the stratospheric concentration of N_2O_5 is important to ozone chemistry; very few measurements of this species exist.

The first tentative observation of stratospheric N_2O_5 was made by Roscoe (1982), who inferred the existence of N_2O_5 from Pressure Modulator Radiometer emission measurements of the ν_{12} band in the 1230-1260 cm^{-1} region. This same band was measured at low spectral resolution (19 cm^{-1}) at predawn by Evans (1986), who inferred the total column amount of N_2O_5 above 30 km. The first unequivocal spectroscopic detection of stratospheric N_2O_5 was made with the Atmospheric Trace Molecule Spectroscopy (ATMOS) instrument with .015 cm^{-1} resolution, measuring absorption by the ν_{12} band (Toon et al., 1986), and by the ν_1 and ν_{11} bands (Toon, 1987). The ATMOS results, taken at sunrise and sunset, observed a strong diurnal variation in N_2O_5 . The present work yields the first N_2O_5 altitude distributions obtained for the period from midnight to sunrise.

Experimental

The instrumentation employed consists of a liquid nitrogen-cooled Michelson interferometer

(SIRIS) with liquid helium-cooled Si-Ga detectors. The maximum optical path difference for the interferometer is 22.8 cm, giving an apodized spectral resolution of 0.044 cm^{-1} . This high spectral resolution is necessary to isolate the molecular continuum of N_2O_5 from the strong features of the more abundant radiatively active stratospheric gases. Four narrow spectral channels, selected principally in the atmospheric windows free of major CO_2 and O_3 emission, are observed simultaneously: (1) 700-960, (2) 1230-1350; (3) 1550-1650, and (4) 1840-1940 cm^{-1} . Individual spectra are acquired with integration times of 2-3 minutes. An overview of the limb emission spectra has been given by Kunde et al. (1987), with results on trace gas concentrations by Abbas et al. (1987) and Massie et al. (1987). Fifteen gases (CO_2 , O_3 , CFCl_3 , CF_2Cl_2 , CHF_2Cl , CCl_4 , H_2O , CH_4 , CF_4 , HNO_3 , N_2O , NO_2 , ClONO_2 , N_2O_5 , NO) have been identified to date.

The concentration of N_2O_5 , the subject of this paper, is derived from channel 2 measurements of the ν_{12} band. The data used are from a flight from the National Scientific Balloon Facility (NSBF) in Palestine, Texas on September 15-16, 1986. The float altitude was ~ 39.7 km. The infrared spectra were recorded from midnight to $\sim 05:45$ am. The instrument field of view is 0.5° , giving an altitude resolution of ~ 3 km. The instrument pointing has been verified using CO_2 lines in the 700-810 cm^{-1} region of channel 1. The original calibration for channel 2 used measurements of on-board blackbodies. Subsequent comparisons of observed and synthetic spectra for CH_4 lines indicated a discrepancy in the original calibration due to a non-linearity in the calibration. The probable cause of this effect is a non-linearity in the feedback resistor in the channel 2 preamplifier. To correct the original calibration, the observed CH_4 radiances were adjusted to match synthetic values. The final calibration of channel 2 thus depends on an assumed mid-latitude CH_4 vertical distribution (WMO, 1985). An estimate of the error from this assumption has been made. A 1σ error in the CH_4 mixing ratio ranging from 10% at 20 km to 20% at 40 km yields an average 1σ radiance error of 8%. As will be seen in the error analysis, this error source is not significant.

Data Analysis

The altitude profile of N_2O_5 has been derived from sets of averaged spectra. Averaging was used because: (1) post-facto pointing from CO_2 lines has not yet been established for individual scans, only for the averages; and, (2) not all

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limb sequences are complete. Four time periods of averaged data were chosen for each angle: (1) 0:00–01:10 am (midnight), (2) 2:15–3:25 am, (3) 04:15–05:45 am (predawn), and (4) the entire nighttime from 0:00–05:45 am (grand). The averages for the first three time periods contain 1, 2 or 3 spectra. The grand averages are shown at the apodized resolution of .044 cm⁻¹ in Figure 1 for tangent heights (H_T) of 36, 31, 28, and 24 km. The number of spectra in each grand average is 10, 5, 6, and 8 for Figures 1a through 1d, respectively. The broad continuum emission feature appearing between 1235–1260 cm⁻¹, peaking around 1245 cm⁻¹, is due to the ν₁₂ band of N₂O₅. Since the spectrum of N₂O₅ is not resolved at .044 cm⁻¹ resolution (Murchay and Goldman, 1981), only the continuum envelope is available for the identification of N₂O₅. Strong emission lines of N₂O and CH₄ are seen superimposed on the N₂O₅ continuum. Error bars (1σ) are shown on each average at 1252 cm⁻¹, near the peak of the N₂O₅ emission feature. The standard deviation in the continuum at 1252 cm⁻¹ ranges from 36% for H_T = 36 km, where there is little continuum, to 13% for H_T = 24 km (Table 1). The standard deviation spectrum arises mainly from jitter in the pointing, instrument noise, changes in the temperature during the night, and changes in the N₂O₅ mixing ratio, which is increasing through the night.

Figures 2a and 2b illustrate the effect of N₂O₅ on the emission spectrum; the synthetic spectrum was generated using the mixing ratio of N₂O₅ inferred from the grand average spectra.

The observed N₂O₅ feature and the corresponding standard deviation spectrum (STD) for the nighttime grand average spectrum for H_T = 31 km is shown in detail in Figures 2c and 2d, respectively. The 1σ standard deviation spectrum was derived from the 5 individual spectra in this average. The 1σ error bar (from Figure 2d) is also illustrated in Figure 2c for 1252 cm⁻¹. Only the 1250–1260 cm⁻¹ region is used in the N₂O₅ analysis; the continuum in the 1235–1250 cm⁻¹ region is less reliable as it is near the edge of the channel 2 response. The observed spectra are distortion free for wave numbers greater than 1250 cm⁻¹ as evidenced in the standard deviation spectrum (Figure 2d). The continuum baseline is essentially flat and corresponds to the instrument noise. Baseline distortions, if present, would increase the overall noise level

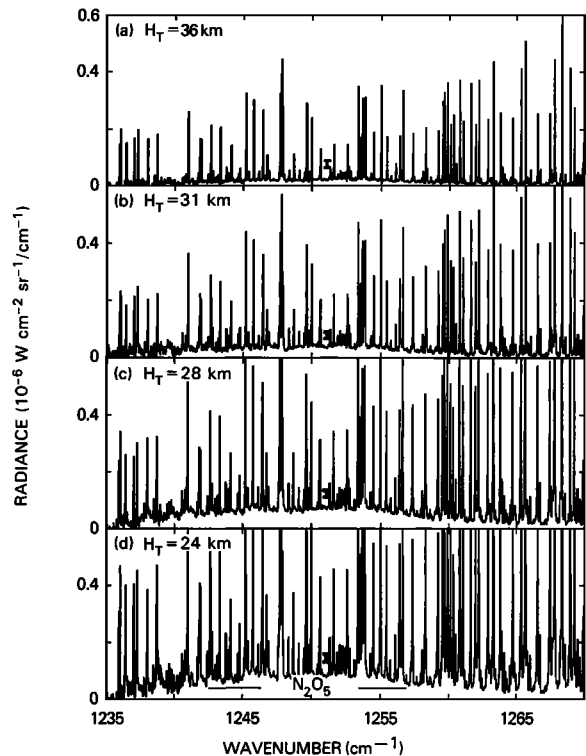


Fig. 1. Limb sequence exhibiting continuum emission by N₂O₅ in the 1235–1260 cm⁻¹ region at 0.044 cm⁻¹ apodized resolution. The spectra represent grand averages for the nighttime from midnight to predawn.

and cause the standard deviation spectrum to deviate from flatness.

The mixing ratio profile of N₂O₅ was retrieved from the averaged spectra using the least-squares relaxation method described in Shaffer et al. (1988). The retrieval method used 10 mesh points (illustrated by arrows in Figure 2c) between 1250 and 1259 cm⁻¹ in the isolated regions between the resolved emission lines. These points are in the N₂O₅ continuum envelope near the emission peak; thus maximizing the retrieval sensitivity. At each tangent height, the retrieval method determines the N₂O₅ mixing ratio which minimizes the residual sum of squares for the 10 mesh

Table 1. Precision and Accuracy of Observed Radiances

H _T (km)	Observed Radiance Random Error (1σ)		Systematic (%)	Total Error (1σ) (%)
	W cm ⁻² sr ⁻¹ /cm ⁻¹	%		
38	.006 × 10 ⁻⁶	54	20	58
36	.009 × 10 ⁻⁶	36	20	41
31	.009 × 10 ⁻⁶	22	20	30
28	.012 × 10 ⁻⁶	16	20	26
24	.011 × 10 ⁻⁶	13	20	24
22	.011 × 10 ⁻⁶	11	20	23

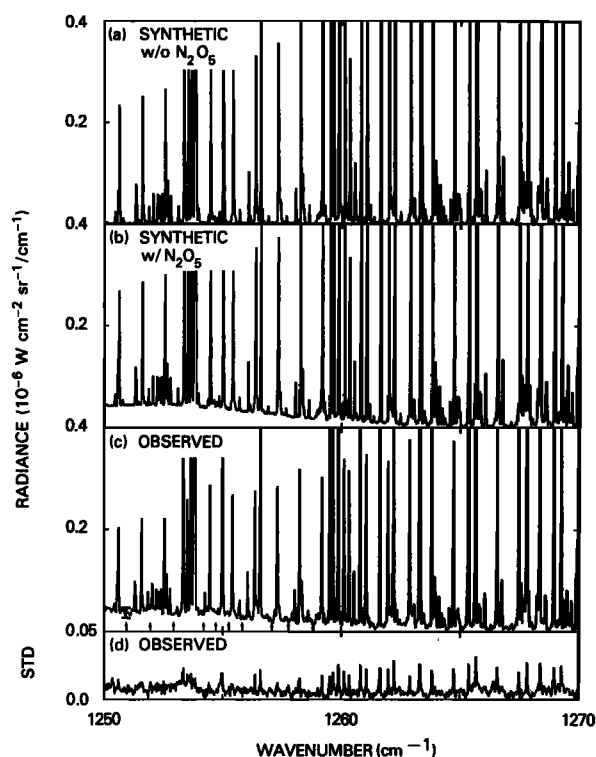


Fig. 2. Grand average spectrum for $H_T = 31$ km. Panels (a) and (b) illustrate the effect of N₂O₅ emission on the synthetic spectrum. Panels (c) and (d) are the observed spectrum and the corresponding 1σ standard deviation.

points. The temperature profile used in the retrieval was from National Meteorological Center soundings near the balloon's ground track. Vertical distributions for N₂O, H₂O, and O₃, included in the retrieval calculation, were taken from an early November 1984 flight from Palestine, Texas (Abbas et al., 1987).

Laboratory absorption coefficients for N₂O₅ have been determined from room temperature laboratory transmittance measurements (Massie et al., 1985). To improve the accuracy of retrievals low temperature laboratory measurements have been made at NCAR (Cantrell et al., 1988). The absorption coefficients were found to be temperature insensitive over the range of our balloon observations. Thus, the room temperature absorption coefficients of Massie et al., (1985) were used for the N₂O₅ retrieval; the peak absorption cross section is $1.9 \times 10^{-18} \text{ cm}^2/\text{molecule}$ and the integrated band intensity is $3.8 \times 10^{-17} \text{ cm}^2 \text{ molecule}^{-1} \text{ cm}^{-1}$. The corresponding values at 233K are 1.9×10^{-18} and 4.0×10^{-17} , respectively (Cantrell, et al., 1988).

The inferred mixing ratios, along with the error bars determined from the retrieval from the grand average, are shown in Figure 3. The error bars for the N₂O₅ mixing ratio have been determined from the inversion algorithm using the total radiance errors listed in Table 1. The uncertainty in the retrieved N₂O₅ mixing ratio was obtained by determining the range of mixing ratio values at each altitude which give synthetic spectra lying within one standard deviation of the observed spectrum. The sources

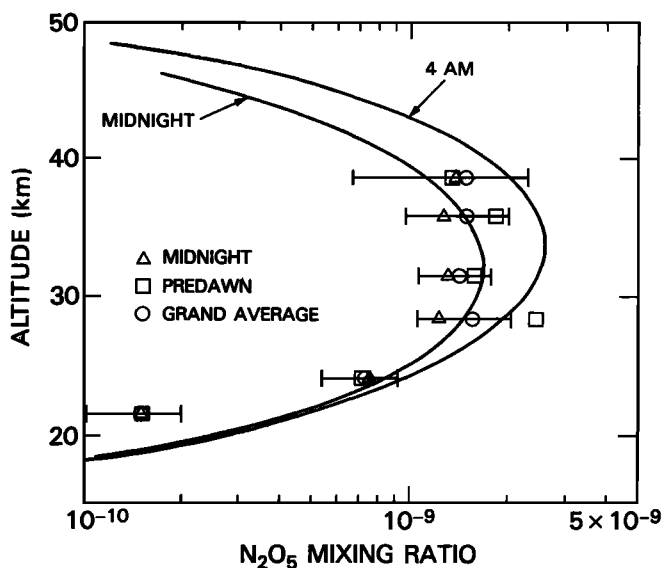


Fig. 3. Comparison of retrieved N₂O₅ concentration profiles with 1-D photochemical predictions for midnight and predawn. The profile for the grand average is also included with 1σ error bars.

of error affecting both the precision (random) and accuracy (systematic) of the results were considered. The total error bars in Table 1 representing the 1σ uncertainty are the quadrature sum of the random errors derived from the observed spectra, and the systematic errors due to the molecular parameters.

The random component was derived from the standard deviation of the grand average spectrum. This component includes all sources of error occurring during the 6 hours of flight at night; pointing jitter, instrument noise, temperature and mixing ratio changes in time and spatial location. This noise level is 5×10^{-9} to $1 \times 10^{-8} \text{ W cm}^{-2} \text{ sr}^{-1} \text{ cm}^{-1}$, and is primarily due to instrument noise. The jitter in pointing is estimated to be $\pm 0.03^\circ$ from CO₂ lines in the 700–820 cm^{-1} region of channel 1. The error from this source is $\sim 3\%$ for tangent heights around float height (40 km) and 10% for tangent heights in the 20 km region. The precision of the observed radiances is dominated by instrument noise for the high altitudes. At the low altitudes (~ 20 km), both instrument noise and pointing jitter contribute to the precision.

The systematic error was estimated at 20%, due to the uncertainty in N₂O₅ band strength (Cantrell, et al., 1988). Other systematic errors, such as pointing accuracy, are believed to be small and difficult to assess.

Discussion

The inferred mixing ratios for the midnight to predawn time intervals, along with the correspondingly 1-D photochemical predictions (Herman 1979; Herman and McQuillan, 1985) are shown in Figure 3. The model predictions indicate that the percent variation of N₂O₅ from midnight to dawn is smallest at low altitudes (20 km), and increases steadily with height up to the balloon float altitude (~ 40 km).

The diurnal aspect of these results will be discussed first. The retrieved mixing ratios show good internal consistency increasing from midnight to predawn for the upper stratosphere ($H_T > 25$ km), with no observed changes in the lower stratosphere. These observed diurnal changes are in general accordance with the photochemical predictions. The retrieved N₂O₅ values at 38 km are an exception; however, the error bars are large at this altitude due to the small N₂O₅ continuum. The magnitude of the observed changes in N₂O₅ with local time is roughly in agreement with the theoretical change; however, this conclusion can only be tentative due to the magnitude of the error bars. The predicted increase in N₂O₅ from midnight to predawn is too small to be credibly measured with these observations. Future flights will strive for greater accuracy in order to quantitatively measure N₂O₅ changes for the midnight to predawn period.

The second aspect of the comparison in Figure 3 concerns the overall agreement between theory and observations. On this basis, the observing mixing ratios are less than the predicted values, with the exception of the observations at 28 km.

The best previous measurements of N₂O₅ concentrations were made by the ATMOS experiment (Toon et al., 1986). As shown in Figure 4, the SIRIS results are consistent with the preliminary ATMOS N₂O₅ profile.

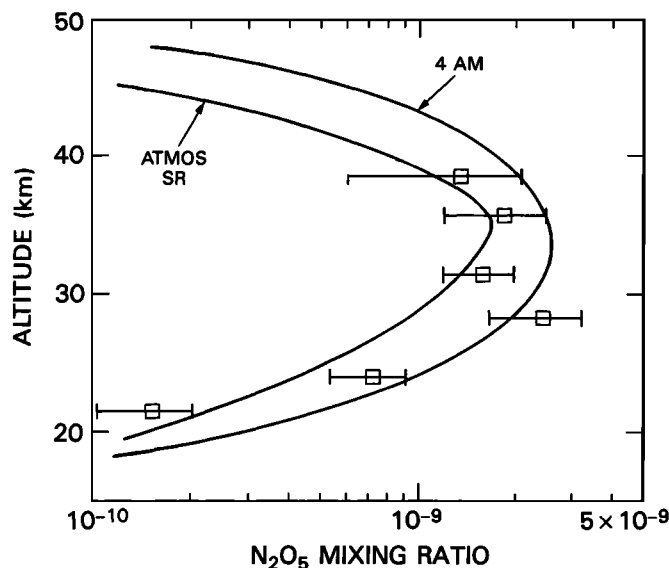


Fig. 4. Comparison of N₂O₅ concentration profiles for SIRIS at predawn and ATMOS at sunrise.

Conclusions

The main conclusions are: (1) The vertical profile of N₂O₅ has been determined for the 20–40 km altitude range over the midnight to predawn timeframe; (2) The observed profiles are generally lower than 1-D photochemical predictions; and, (3) The inferred profiles for upper altitudes (> 25 km) generally indicate N₂O₅ increasing toward predawn; however, the error

bars are presently too large to demonstrate this quantitatively.

Future flights will emphasize improving instrument sensitivity for greater accuracy and longer flights to obtain the full diurnal cycle.

References

- Abbas, M. M. et al., Simultaneous measurements of stratospheric O₃, H₂O, CH₄, and N₂O profiles from infrared limb thermal emissions, *J. Geophys. Res.*, **92**, 8343–8353, 1987.
- Cantrell, C. A. et al., Infrared absorption cross sections for N₂O₅, *Chem. Phys. Letters*, in press, 1988.
- Evans, Wayne, F. J., Observations of the 8 μ m N₂O₅ thermal emission feature in the stratosphere, *Appl. Opt.*, **25**, 1866–1868, 1986.
- Herman, J. R., The problem of nighttime stratospheric NO₃, *J. Geophys. Res.*, **84**, 6336–6338, 1979.
- Herman, J. R. and C. McQuillan, Atmospheric chlorine and stratospheric ozone: Nonlinearities and trend detection, *J. Geophys. Res.*, **90**, 5721–5732, 1985.
- Kunde, V. G. et al., Infrared spectroscopy of the lower stratosphere with a balloon-borne cryogenic Fourier spectrometer, *Appl. Opt.*, **26**, 545–553, 1987.
- Massie, S. T., A. Goldman, D. G. Murcray, and J. C. Gille, Approximate absorption cross sections of F₁₂, F₁₁, ClONO₂, N₂O₅, HNO₃, CF₄, F₂₁, F₁₁₃, and F₁₁₄, *Appl. Opt.*, **24**, 3428, 1985.
- Massie, S. T. et al., Atmospheric infrared emission of ClONO₂ observed by a balloon-borne Fourier spectrometer, *J. Geophys. Res.*, **92**, 14,806–14,814, 1987.
- Murcray, D. G. and A. Goldman, Handbook of high resolution infrared laboratory spectra of atmospheric interest, CRC Press, Boca Raton, Florida, 1981.
- Roscoe, H. K., Tentative observation of stratospheric N₂O₅, *Geophys. Res. Lett.*, **9**, 901–902, 1982.
- Shaffer, W. A., V. G. Kunde, and B. J. Conrath, Retrieval of constituent mixing ratios from limb thermal emission spectra, *Appl. Opt.*, in press, 1988.
- Toon, G. C., C. B. Farmer, and R. H. Norton, Detection of stratospheric N₂O₅ by infrared remote sounding, *Nature*, **319**, 570–571, 1986.
- Toon, G., Reply: Detection of stratospheric nitrogen species, *Nature*, **330**, 427, 1987.
- World Meteorological Organization, Atmospheric Ozone 1985, Report No. 16, Vol. 1, NASA/GSFC, Code 610, Greenbelt, MD, 20771, p. 88–99, 1985.

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