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Infrared Emission Measurements of Morning Stratospheric N₂O₅

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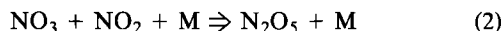
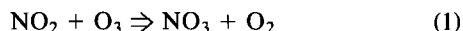
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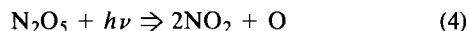
Infrared emission spectra obtained during a balloon flight of the Air Force Geophysics Laboratory SCRIBE system by the University of Denver are used to measure stratospheric N₂O₅ after sunrise over New Mexico (latitude 33°N). This is the first daytime measurement of N₂O₅. Comparisons with photochemical modeling show consistency between the observed and predicted decline of N₂O₅ during the morning hours.

INTRODUCTION

N₂O₅ is an important stratospheric reservoir species for NO_x, produced during the night by the reactions



After sunrise, N₂O₅ gradually photolyzes back into NO₂:



The diurnal variation of stratospheric N₂O₅, as computed in photochemical models [Brasseur and Solomon, 1984], is a periodic function; it decays due to photolysis after sunrise and increases through reaction (2) at night.

Nighttime N₂O₅ was tentatively observed by Roscoe [1982] and Evans [1986]. A definitive observation of N₂O₅ was made by Toon *et al.* [1986] and Toon [1987], who observed the ν_{12} band (~1230–1260 cm⁻¹) and the ν_1 and ν_{11} bands (~1680–1770 cm⁻¹) in transmission spectra obtained with the ATMOS instrument at sunrise. Recently, Kunde *et al.* [1988] have measured nighttime N₂O₅ from infrared emission spectra in the ν_{12} region.

In the present work, infrared emission data are analyzed to demonstrate the first measurement of daytime N₂O₅, and the results are compared with the predictions of a one-dimensional photochemical model.

OBSERVATIONS

The data were obtained during a balloon flight of the Air Force Geophysics Laboratory (AFGL) SCRIBE system (Stratospheric Cryogenic Interferometer Balloon Experiment) by the University of Denver from Roswell, New

Mexico, on July 5, 1984. The instrumentation consisted of a LN₂-cooled Michelson interferometer system employing cat's eye optics and having a maximum path difference of ~9 cm. The time for a single scan was ~30 s, including a 5-s fly-back. The field of view was ~0.8°. Data for the radiometric calibration of the emission spectra were recorded during the flight by occasionally moving an on-board black body into the instrument field of view. For a detailed discussion of the SCRIBE instrumentation, see Murcray *et al.* [1984].

The balloon was launched at 0610 MDT (Mountain Daylight Time), and reached a float altitude of 30.6 km at 0740 MDT. Data were recorded at a number of zenith angles. Of these, the scans at 90.6° and 91.1° were selected as most suitable for the detection and measurement of daytime N₂O₅. The 90.6° data displayed here are actually the average of 14 individual scans selected from those recorded between 0751 and 0759 MDT, while the 91.1° data are the average of 12 scans recorded during the interval 0916–0923.5 MDT. Sunrise occurred at the balloon float altitude at approximately 0530 MDT, and at ground level at the local time of 0456 MST (Mountain Standard Time).

ANALYSIS AND RESULTS

The data were analyzed by comparison with synthetic spectra generated using a line-by-line computer program developed at the University of Denver. The program, which takes refractive effects into account through a ray-tracing routine, calculates transmittance or emission over a user-selected number of atmospheric layers at a net interval of 0.001 cm⁻¹. The 1986 edition of the HITRAN data base [Rothman *et al.*, 1987] is used as input to the program. Line parameters for N₂O₅ do not exist, but the absorption coefficients needed to compute the N₂O₅ contribution to the atmospheric emission are generated by the program using the absorption cross sections for N₂O₅ which are also included in the HITRAN data base. Finally, the computed radiances are degraded in resolution by convolution with an appropriate instrument line shape function.

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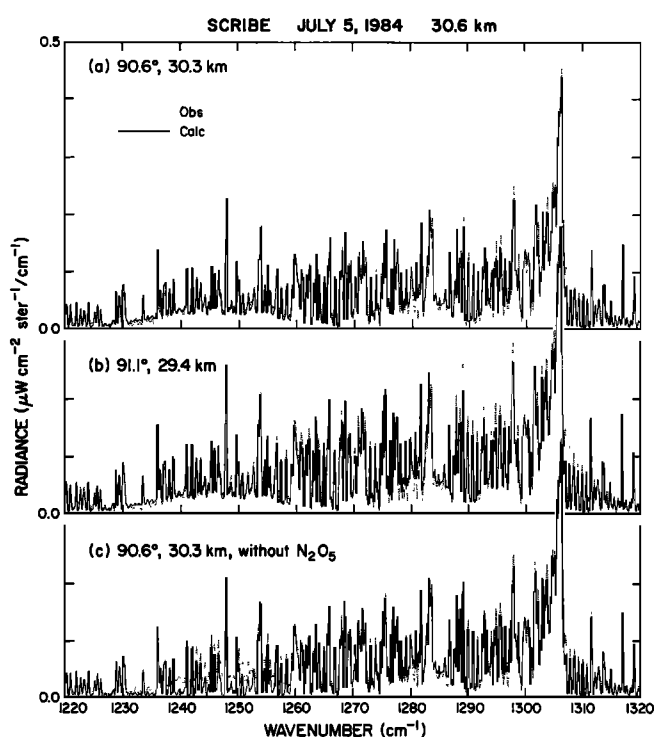


Fig. 1. Comparisons of observed (dotted curves) and calculated (solid curves) atmospheric emission spectra in the 1220–1320 cm^{-1} region. The spectra were obtained during a balloon flight made on July 5, 1984, by the University of Denver with the AFGL SCRIBE system from balloon float altitude of 30.6 km. Zenith angles and tangent altitudes are indicated in the figure. The top two frames include N₂O₅ in the spectral calculations while for the bottom frame N₂O₅ was excluded from the calculation.

Residual background radiance was present at both observation angles (0.06 and 0.08 $\mu\text{W cm}^{-2} \text{sr}^{-1}/\text{cm}^{-1}$ at 90.6° and 91.1°, respectively). For the present analysis the data were adjusted by applying a wavelength dependent correction, described by a linear function such that theory and observation agreed in the “mini windows” centered at 1227.0 and 1267.07 cm^{-1} and at the N₂O-CH₄ blend at 1268.31 cm^{-1} . These three positions are away from significant N₂O₅ absorption. The peak N₂O₅ cross section is $1.90 \times 10^{-18} \text{ cm}^2$ at 1246 cm^{-1} (with no temperature correction), whereas the cross sections for the three calibration points are $\leq 1.5 \times 10^{-19} \text{ cm}^2$. Validity of the adjustment is apparent in the reasonable agreement to the CH₄ spectrum longward of 1268 cm^{-1} and insensitivity of the N₂O₅ quantification to the background radiance. Subsequently, a least squares fitting for N₂O₅ amounts over the 1240–1247 cm^{-1} interval (with N₂O and CH₄ fixed) was made. Recent measurements of N₂O₅ cross sections [Cantrell *et al.*, 1988b] show 1.79×10^{-18} and $1.82 \times 10^{-18} \text{ cm}^2$ at 1246 cm^{-1} for 298 and 233K, respectively. Due to the small differences in comparison to the (room temperature) HITRAN value and the small temperature dependence, we did not adjust the HITRAN values.

The pressure-temperature profile used in these simulations was taken from a radiosonde ascent from White Sands Missile Range at 0800 MDT on the same day as the balloon flight. Mixing ratio profiles for the various constituents (except N₂O₅) are from Smith [1982].

Figures 1a and 1b show a comparison between the calculated (solid curve) and observed (dotted curve) emission for

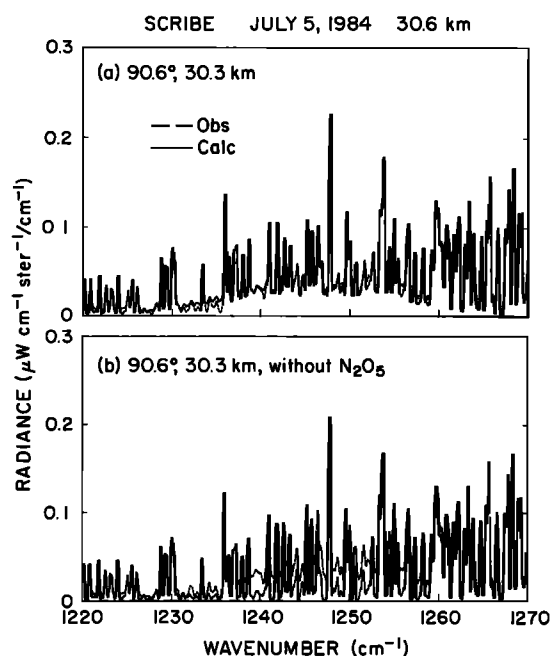


Fig. 2. Comparison of observed (dotted curves) and calculated (solid curves) atmospheric emission spectra in the N₂O₅ 1220–1270 cm^{-1} region. Figures 2a and 2b are expanded versions of Figures 1a and 1c.

zenith angles of 90.6° and 91.1°, respectively. (Tangent heights are 30.3 km and 29.4 km.) The data have been smoothed by a triangular filter to 0.25 cm^{-1} resolution. The region is dominated by sharp emission lines of CH₄, N₂O, H₂O, and, to a considerably lesser extent, CO₂. At lower zenith angles there are also contributions from HNO₃ above $\sim 1280 \text{ cm}^{-1}$, as well as from CF₄ ($\sim 1283 \text{ cm}^{-1}$) and ClONO₂ ($\sim 1292 \text{ cm}^{-1}$), but these molecules do not contribute appreciably at the zenith angles shown here. The broad, smooth emission feature in Figure 1a and 1b from 1230 to 1260 cm^{-1} is due to stratospheric N₂O₅. This can be seen from Figure 1c, which is the same as Figure 1a, except that no N₂O₅ has been included in the calculation. Figure 2 shows an expanded plot of the N₂O₅ 1220–1270 cm^{-1} region from Figures 1a and 1c. Figure 3 presents the observed

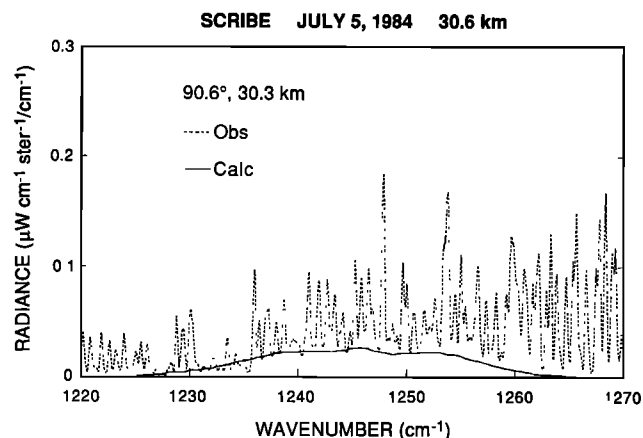


Fig. 3. Observed emission spectra (dotted curves) and theoretical calculation (solid curve) only including the N₂O₅ contribution.

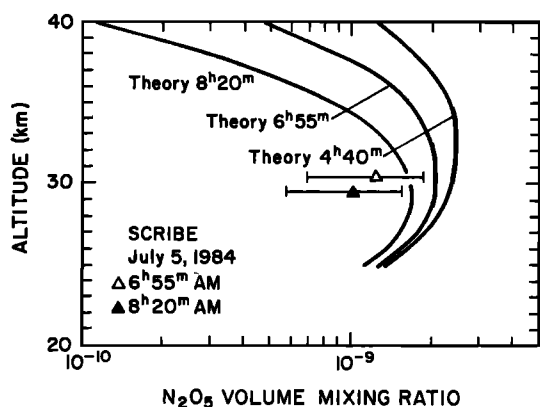


Fig. 4. One-dimensional photochemical-transport model (see text) mixing ratio profiles (solid curves) of N₂O₅ for predawn (0440 MST) and morning conditions used for comparison with the experiment. The triangles show the measured N₂O₅ mixing ratios 1.26 and 1.04 ppb, at the tangent altitudes 30.3 and 29.4 km.

radiance at 90.6° and a theoretical calculation which only includes the contribution due to N₂O₅.

The synthetic spectra of Figures 1a and 1b were computed using N₂O₅ profiles of the same general shape as the solid curves of Figure 4, which are generated as described below, multiplied by a scaling factor. The triangles in Figure 4 show the resulting N₂O₅ mixing ratios, 1.26 and 1.04 ppb, at the tangent altitudes of the two scans, 30.3 and 29.4 km, respectively. Theoretical N₂O₅ mixing ratios are 2.10 and 1.65 ppb for the corresponding times of 0655 and 0820 MST. The observed relative decrease in N₂O₅ is therefore 0.83, whereas the theoretical value is 0.79. The estimated accuracy of the absolute N₂O₅ measurements is ±45%. This is based on uncertainties in radiance calibration and pointing (10%), vertical slope of the theoretical N₂O₅ mixing ratios (10%), spectral line parameters (15%), and the N₂O, CH₄ profiles (10%). Error in the observed relative change is estimated as ±15% (due to partial cancellation of systematic errors).

The theoretical N₂O₅ mixing ratios curves were calculated by a one-dimensional photochemical transport model [Cicerone *et al.*, 1983]. The time dependent calculation extended between 10 and 80 km altitude. The pressure-temperature profile was that mentioned above, and the solar declination of +23° and the latitude of +33° matched that for the balloon flight.

Reaction rates for 81 two- and three-body gas-phase processes and 25 photolysis processes for 38 gaseous species follow that of the Jet Propulsion Laboratory (JPL 1987) [DeMore *et al.*, 1987], but with the Cantrell *et al.* [1988b] equilibrium constant for reaction (2). At 30 km at a temperature of 231K, the Cantrell and JPL 1987 equilibrium constants differ by 27%. However, for the geometry of the July 5 observation, the rate of thermal decomposition of N₂O₅ is slower than the diurnal average of N₂O₅ photolysis by a factor of 78, so the influence of the revised equilibrium constant upon the N₂O₅ mixing ratio is small. The total odd-chlorine (Cl + ClO + HOCl + ClONO₂ + HCl + ClO₂) mixing ratios are 2.17 and 2.61 ppb at 30 and 60 km, respectively. The *J* values at 30 km are $3.42 \times 10^{-5} \text{ s}^{-1}$ and $5.78 \times 10^{-5} \text{ s}^{-1}$ for N₂O₅ photolysis (reactions (3) and (4)) for 0655 and 0820 MST, respectively. The albedo value was

0.35, and *J* is insensitive to changes in the albedo (e.g., *J* equals $5.62 \times 10^{-5} \text{ s}^{-1}$ for an albedo of 0.25 at 0820 MST).

Since N₂O₅ is but one member of the NO_y family (N + NO + NO₂ + NO₃ + HNO₃ + HNO₄ + 2*N₂O₅ + ClONO₂), the theoretical value of N₂O₅ is related to the total NO_y mixing ratio. For the theoretical curves of Figure 2, NO_y is equal to 15.0 and 14.3 ppb at 40 and 30 km, respectively. Observations of Russell *et al.* [1988] for May 1985, sunset, 30°N latitude indicate NO_y near 16.7 and 15.2 ppb at 40 and 30 km, roughly 11% higher than our one-dimensional theoretical predictions.

The model N₂O₅ and NO_y profiles are reasonable, though they may not accurately represent the mixing ratio profiles of July 5, 1984, due to seasonal variations and model limitations. Differences between one- and two-dimensional models are illustrated, for example, in Figure 10-58 of World Meteorological Organization (WMO)/NASA [1986], in which the two modeling techniques at 30 km estimate different amounts of NO_y and, presumably, different amounts of N₂O₅. Despite such differences, the present measurement of the relative change of N₂O₅ during the morning hours is consistent with the temporal change of the one-dimensional calculation. Our observed early morning decline in N₂O₅ concentration is also consistent qualitatively (see equations (1)–(4)) with measured early morning increases in both NO and NO₂ [e.g., Ridley *et al.*, 1977; Flaud *et al.*, 1988; Rinsland *et al.*, 1988].

The present morning N₂O₅ results and the sunrise and nighttime N₂O₅ observations by Toon *et al.* [1986] and Kunde *et al.* [1988], all report N₂O₅ mixing ratios in the 1- to 2-ppb range near 30 km altitude. One sees that our observed mixing ratios at 0755 MDT and 0920 MDT are ~60% smaller than the values predicted by our model. Kunde *et al.* [1988] showed that their observed nighttime N₂O₅ is 20–30% smaller in comparison to a (different) photochemical model. However, the relative decrease of 0.83 over the 1.5 hours between the observations is consistent with that of 0.79 predicted by the model. The relative decrease in N₂O₅ concentration during the morning can be approximated by $D = \exp(-J \Delta t)$, where *J* is the average N₂O₅ photolysis rate over the time interval Δt . With $J = 4 \times 10^{-5} \text{ s}^{-1}$ and $\Delta t = 1 \text{ hour } 25 \text{ min}$, $D = 0.81$, in good agreement with the detailed model results of 0.79. *D* is not sensitive to the actual N₂O₅ amount, and thus the absolute difference between models and measurements of N₂O₅ is less important than the temporal variations.

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