

Validation of SAGE II NO₂ Measurements

D. M. CUNNOLD,¹ J. M. ZAWODNY,² W. P. CHU,² J. P. POMMEREAU,³ F. GOUTAIL³
 J. LENOBLE,⁴ M. P. MCCORMICK,² R. E. VEIGA,² D. MURCRAE,⁵ N. IWAGAMI,⁶
 K. SHIBASAKI,⁷ P. C. SIMON,⁸ AND W. PEETERMANS⁸

Stratospheric aerosol and gas experiment (SAGE) II satellite-borne measurements of the stratospheric profiles of NO₂ at sunset have been made since October 1984. The measurements are made by solar occultation and are derived from the difference between the absorptions in narrow bandwidth channels centered at 0.448 and 0.453 μm . The precision of the profiles is approximately 5% between an upper altitude of 36 km and a latitude-dependent lower altitude at which the mixing ratio is 4 ppbv (for example, approximately 25 km at mid-latitudes and 29 km in the tropics). At lower altitudes the precision is approximately 0.2 ppbv. The profiles are nominally smoothed over 1 km except at altitudes where the extinction is less than $2 \times 10^{-5}/\text{km}$ (approximately 38 km altitude), where 5 km smoothing is employed. The profile measurement noise has an autocorrelation distance of 3–5 km for 1 km smoothing and more than 10 km for 5 km smoothing. The absolute accuracy of the measurements is estimated to be 15% based on uncertainties in the absorption cross-sections and their temperature dependence. Comparisons against two sets of balloon profiles and atmospheric trace molecules spectroscopy experiment (ATMOS) measurements show agreement within approximately 10% over the altitude range of 23 to 37 km at mid-latitudes. SAGE II NO₂ measurements are calculated to be approximately 20% smaller at the mixing ratio peak than average limb infrared monitor of the stratosphere (LIMS) measurements in the tropics in 1979. They show acceptable agreement with SAGE I sunset NO₂ measurements in the tropics in 1979–1981 when the limited resolution and precision of the SAGE I measurements and the differences between the two measurement techniques are considered.

1. INTRODUCTION

The stratospheric aerosol and gas experiment (SAGE) II instrument was launched from the space shuttle on October 5, 1984. It was maneuvered into a 610-km circular orbit with an inclination of 56°. The instrument is a seven channel Sun photometer which makes measurements at the wavelengths of 1.02, 0.94, 0.60, 0.525, 0.453, 0.448, and 0.385 μm . The instrument scans back and forth across the solar disk as the Sun is occulted by the Earth's atmosphere. One product of these measurements is NO₂ profiles at a 90° solar zenith angle (sunrises and sunsets) at the points where the line of sight from the instrument to the Sun are tangential to the Earth's atmosphere. The instrument field of view in the direction normal to the line of sight is 0.5 km vertically by 2.5 km horizontally.

NO₂ profiles are retrieved on the basis of the difference between the measured irradiances at 0.448 and 0.453 μm (i.e., a differential technique). Using two wavelengths produces good separation of the NO₂ absorption signature from that of other gases and scatterers and makes the technique conceptually similar to the NO₂ measurement technique (which however utilizes many more wavelengths) which has

been used to produce many years of ground-based NO₂ measurements [e.g., Noxon, 1979, 1980; Johnston and McKenzie, 1988] and more recently to make balloon-borne NO₂ measurements [e.g., Pommereau et al., 1987]. Contributions from ozone, aerosols, and neutral density must be removed before the NO₂ profiles can be obtained. The latitude of the NO₂ profiles (and the other atmospheric constituents, aerosols, ozone, and water vapor) observed by SAGE II change from one day to the next such that sampling of the global atmosphere between approximately 70°N and 70°S is produced over a 1-year period (see Figure 1). The orbit of SAGE II is such that the coverage of the global atmosphere is exactly repeated each 364.44 days. The SAGE II data are processed at NASA Langley Research Center, Hampton, Virginia, and are being archived at the National Space Science Data Center (NSSDC) at NASA Goddard Space Flight Center, Greenbelt, Maryland.

The objective of this report is to test the validity of the SAGE II NO₂ measurements within the measurement accuracy of approximately 15%. This is also the estimated (approximate) accuracy of the measurement systems against which the SAGE II NO₂ measurements will be compared. There are, unfortunately, only a few (almost) coincident balloon-borne measurement of NO₂, and thus validation must also depend upon comparisons against climatological distributions of NO₂ and on the self-consistency of the observations.

2. NO₂ RETRIEVALS

The general procedure for retrieving constituent profiles from the SAGE II irradiance measurements is described by Chu [1989] and Chu et al. [1989]. The algorithm is based on the set of equations:

$$\tau(\lambda_i) = \tau_a(\lambda_i) + a\tau_{\text{O}_3}(\lambda_i) + b\tau_{\text{NO}_2}(\lambda_i) + \tau_r(\lambda_i) \quad (1)$$

¹School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta.

²NASA Langley Research Center, Hampton, Virginia.

³Service d'Aéronomie, CNRS, Verrières le Buisson, France.

⁴Université des Sciences et Techniques de Lille, Cedex, Lille, France.

⁵Department of Physics, University of Denver, Denver, Colorado.

⁶Geophysics Research Laboratory, University of Tokyo, Japan.

⁷Kokugakuin University, Tokyo, Japan.

⁸Institut d'Aéronomie Spatiale, Bruxelles, Belgium.

Copyright 1991 by the American Geophysical Union.

Paper number 91JD01344.
 0148-0227/91/91JD-01344\$05.00

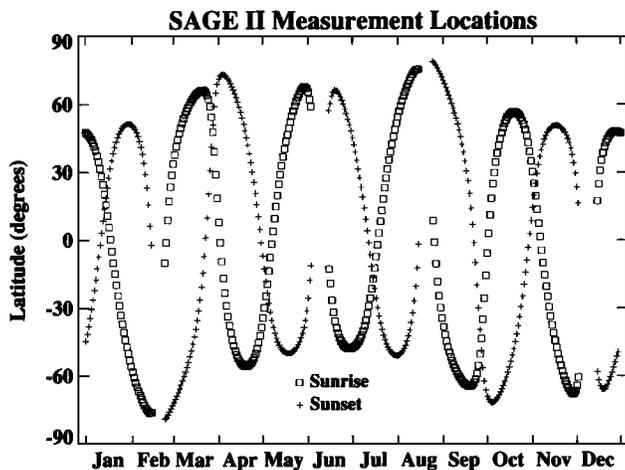


Fig. 1. Latitudes of the SAGE II measurement locations. Each point represents the average of the latitudes for 1 day. Sunrise events are denoted by squares and sunset events by plus signs. The orbit of SAGE II provides repeat coverage of individual measurement location from one year to the next. Large gaps correspond to times when the spacecraft remains fully sunlit and no sunrise/sunset events occur.

where $\tau(\lambda_i)$ is the slant path optical depth at wavelength λ_i and the subscripts a , O_3 , NO_2 , and r denote the contributions from aerosols, ozone, NO_2 , and Rayleigh scatterers, respectively. Here τ_{O_3} and τ_{NO_2} are the optical depths at 0.60 and 0.448 μm , respectively. The constants a_i and b_i are the ratios of the ozone and NO_2 absorption cross sections to the values at 0.60 and 0.448 μm , respectively. Values of a_i and b_i are given in Table 1. At 30 km, which is approximately the level of the maximum NO_2 concentration in the stratosphere, the relative contributions to the optical depth at 0.448 μm are approximately 0.1, 0.3, 1.0, and 2.5 for aerosols, ozone, NO_2 , and Rayleigh scatterers, respectively. Below 25 km the aerosol and Rayleigh contributions are an order of magnitude larger. However, by using the difference in optical depth between the channels centered at 0.448 and 0.453 μm , the NO_2 signal is enhanced and the relative contributions to the difference at 30 km are approximately 0.01, 0.3, 1.0 and 0.6, respectively. Thus the differential absorption analysis procedure, which is utilized at all altitudes, is particularly advantageous for separating the aerosol from the NO_2 contribution to the optical depth below 25 km altitude.

The retrieval commences by removing the contribution from Rayleigh scattering at each wavelength. These contributions are estimated from a knowledge of the tangent altitude of the measurement; this is obtained from the satellite ephemeris data (which is used to obtain a reference

altitude for the profile) combined with instrumental sunscan timing information. The National Weather Service (NWS) provides an atmospheric temperature profile based on interpolation of the location of each SAGE II profile and an atmospheric density profile is then derived by linear interpolation of pressure-height information. In this way the Rayleigh-scattering contribution at each tangent altitude is estimated to an accuracy of approximately 5%.

Next a first guess of the NO_2 slant path column is made on the basis of the difference between the 0.448 and 0.453 μm optical depths. For this purpose the effect of ozone and aerosols is removed using $\tau_a(\lambda_i) = \tau'(\lambda_1)(\lambda_1/\lambda_i)$ and $\tau_{O_3}(\lambda_i) = a_i[\tau'(\lambda_3) - \tau'(\lambda_1)/0.6]$ where the primes indicate that the Rayleigh contributions have been removed from the optical depths. These expressions are based on the absence of absorption by NO_2 and ozone at 1.02 μm and by NO_2 at 0.6 μm ; for this first approximation it is assumed that the aerosol optical depth behaves as λ^{-1} . The resulting NO_2 estimate is then used to remove NO_2 effects from all the channels so that improved estimates of $\tau_{O_3}(\lambda_i)$ and $\tau_a(\lambda_i)$ can be made. The aerosol optical depth estimate is then smoothed in aerosol size distribution space [see *Chu et al.*, 1989]. An improved estimate of the NO_2 slant column can then be made (again on the basis of differential absorption) by removing the revised contributions from ozone and aerosols. Typically, a single iteration of this procedure is sufficient.

The retrieval of an NO_2 profile from the slant path columns is accomplished using an onion-peeling procedure (specifically Twomey's modification of Chahine's nonlinear inversion algorithm [see *Chu et al.*, 1989]). In this procedure a difference between the current measured slant column NO_2 and the previous estimate results in weighted updates of the concentrations at the tangent altitude and at altitudes up to 4 km higher. Solution profiles consist of NO_2 concentrations at 1-km intervals. The maximum extinction for NO_2 is fairly small and to reduce the effects of random noise the profiles are vertically smoothed over 5 km where the extinction is less than $2 \times 10^{-5}/\text{km}$ (typically 38 km altitude and above). Several iterations are made in arriving at the final profile. An algorithm developed independently at the "Laboratoire d'Optique Atmospherique" of Lille, France, gives profiles which agree within the error bars [*Chu et al.*, 1989].

3. NO_2 PROFILE ERRORS

Uncertainties are assigned to each NO_2 profile based on the procedure described by *Russell et al.* [1981]. The error bars include random contributions to the error only. Contributions from four sources are considered: altitude uncertainty, profile temperature errors which affect the removal of the Rayleigh-scattered contributions, errors associated with

TABLE 1. The Seven Wavelengths Used for SAGE II Observations and the Ratios of the Ozone (a_i) and NO_2 (b_i) Absorption Cross Sections to the Ozone Cross Section at 0.6 μm ($5.0678 \times 10^{-21} \text{ cm}^2$) and the NO_2 Cross Section at 0.448 μm ($5.46 \times 10^{-19} \text{ cm}^2$)

	Wavelength, μm						
	λ_1 1.02	λ_2 0.94	λ_3 0.6	λ_4 0.525	λ_5 0.453	λ_6 0.448	λ_7 0.385
a_1	0.0	0.005	1.0	0.439	0.0338	0.0299	0.0
b_1	0.0	0.0	.055	0.348	0.847	1.0	1.14

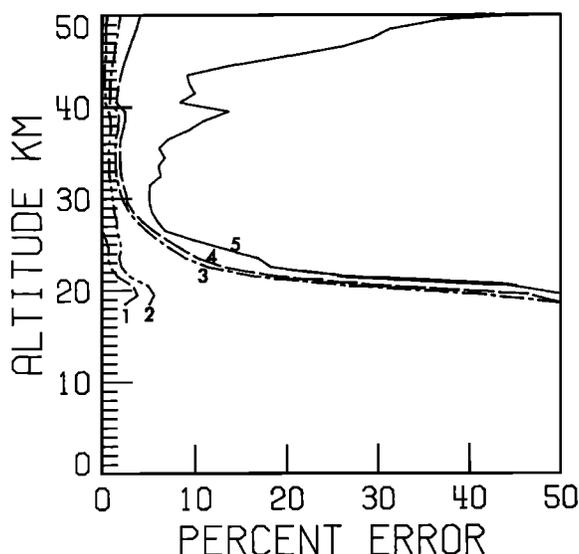


Fig. 2. Height dependence of expected uncertainty accumulated in SAGE II nitrogen dioxide profiles at mid-latitudes showing random contributions resulting from (1) altitude uncertainty, (2) Rayleigh contribution uncertainty, (3) ozone uncertainty, (4) aerosol uncertainty, and (5) measurement uncertainty.

the removal of ozone and aerosols contributions and measurement errors. Measurement errors are a function of the instrument and can be estimated directly from variations in the slant path optical depths as the scan mirror scans back and forth across the Sun. An examination of these errors for the ozone measurements [Cunnold *et al.*, 1988] has suggested that each Sun scan provides statistically independent information. Measurements are taken every 0.5 km in tangent altitude. Thus two measurements/Sun scan contribute to each 1-km level of the solution profile. Therefore the number of independent measurements contributing to a solution profile concentration is the number of Sun scans (approximately six) times a number between 1 and 2 (which reflects the statistical dependency of the measurement noise at 0.5-km intervals and also at larger altitudinal separations). The estimated uncertainty in the optical depth at an individual altitude is then given by the square root of the variance divided by the number of independent measurements. These errors are directly converted to NO₂ profile uncertainties without being mapped through the retrieval algorithm.

The overall random error at each altitude is given by the root sum square of the individual contributions to the error variance. Figure 2 shows these contributions for a typical mid-latitude profile. It may be noted that above 30 km altitude the effects of temperature and reference altitude uncertainties on removing the contribution from Rayleigh scatterers as well as uncertainties in the ozone and aerosol contributions produce error contributions which are small relative to the measurement noise. Between 27 and 36 km altitude the precision of the SAGE II NO₂ measurements is indicated to be approximately 5%. Below approximately 23 km altitude it becomes difficult to separate NO₂, aerosol, and Rayleigh contributions to the optical depth. The cusp in the error profile at approximately 39 km altitude corresponds to the switch from 1 to 5 km smoothing of the profile; this 5 km smoothing has been accounted for in the reported error bars by division by $\sqrt{5}$.

Assumptions about the number of statistically independent irradiance measurements (the error profiles in Figures 2 and 3 and the data tapes are based on $2 \times$ the number of Sun scans) which go into a retrieved NO₂ profile and the effects of the retrieval procedure on these errors may be examined by studying the variances of the retrieved NO₂ concentrations under atmospherically quiescent conditions when measurement noise contributions to NO₂ variability dominate those from atmospheric variability. This should at least provide an upper limit to possible measurement noise contributions. Profiles obtained in the tropics and at mid-latitudes during the summer are chosen for this test. In addition, correlations between SAGE II ozone and NO₂ variations are used to identify and filter out the effects of atmospheric variability during these periods (i.e., only the uncorrelated NO₂ variance is examined). For example, correlation coefficients of approximately -0.5 between O₃ and NO₂ are typically calculated for the 30–35 km altitude range during dynamically active periods (the calculations are actually made on pressure levels). This correlation is found to be associated with primarily horizontal motions of air parcels (a separate manuscript describing the correlations between SAGE II ozone, NO₂, aerosol and temperature variations is in preparation).

Figure 3 shows the profile standard deviations during the selected quiescent months in the first year of SAGE II observations. These were calculated from a version of the data in which the profiles at 1 km altitude intervals were interpolated and replaced by profiles at pressure factor increments of $2^{0.2}$ with level 1 corresponding to 1000 mbar. The altitude corresponding to any level number in the middle and upper stratosphere may be approximately obtained by subtracting three from the level number. The selection of the

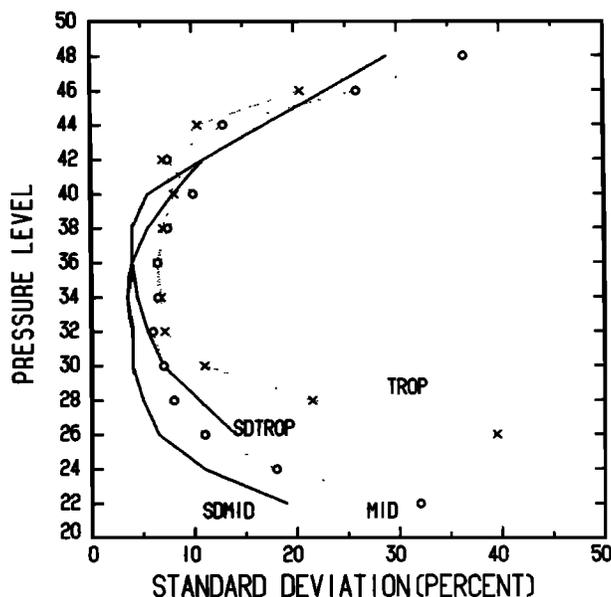


Fig. 3. The standard deviations of SAGE II sunset NO₂ profiles during atmospherically quiescent periods. Latitudinally detrended profiles between $10^\circ \pm 6^\circ\text{N}$ for November 1984, January and July 1985 and $10^\circ \pm 6^\circ\text{S}$ for January and May 1985 were used in the tropics (SDTROP); latitudinally detrended profiles at $50^\circ \pm 6^\circ\text{S}$ and $40^\circ \pm 6^\circ\text{S}$ in January 1985 and $40^\circ \pm 6^\circ\text{N}$ in July 1985 were used for the mid-latitude profiles (SDMID). Mean profile error bars (dashed lines) for these same periods are included for comparison.

TABLE 2. The Vertical Autocorrelations of SAGE II NO₂ Sunset Profiles Averaged Over 10° ± 6°N for November 1984, January and July 1985 and 10° ± 6°S for January and May 1985

Level Number	Pressure, mbar	Correlations		
		1-Level Separation	3-Level Separation	5-Level Separation
28	23.5	0.93	0.54	0.27
30	17.8	0.93	0.56	0.32
32	13.5	0.91	0.50	0.36
34	10.2	0.91	0.50	0.36
36	7.7	0.88	0.47	0.37
38	5.9	0.86	0.52	0.47
40	4.4	0.93	0.80	0.69
42	3.4	0.98	0.91	0.79
44	2.5	0.99	0.91	0.75

The profiles were detrended by latitude and the autocorrelation is tabulated as that between the NO₂ variations at certain levels and the variations at a specified number of levels higher up. The level numbers (minus three) are approximately equivalent to altitude in kilometers.

months included in the tropical profiles in Figure 3 was based on both the absence of a substantial correlation (either positive or negative) with ozone variations during the month and the existence of at least 30 measured profiles in the latitude band. Actually, a result almost identical to that shown in Figure 3 is obtained if all months during the first year with observations in the tropical latitude bands are included. The measured SAGE II NO₂ profile variability takes a minimum value with a standard deviation of less than 5% over a latitude-dependent altitude range from approximately level 39 (~ 36 km) down to the altitude at which the mixing ratio is approximately 4 ppbv (level 32 in the tropics and level 28 at mid-latitudes). Below this altitude the standard deviation of the measurements is approximately 0.2 ppbv. At the lower altitudes, which are typically below the NO₂ concentration peak, the molecular scattering contribution to the received signal is sufficiently large that it becomes more difficult to separate the NO₂ contribution from that due to molecular scattering, and thus the measurement/retrieval uncertainty is indicated as an uncertainty in the NO₂ mixing ratio. Above 36 km altitude the profile standard deviations at all latitudes, expressed as a percentage of the zonal mean mixing ratio, increase approximately linearly with altitude at a rate of approximately 3% per kilometer.

The NO₂ measurement noise inferred from these and other profiles provide important ancillary information to the average profile precisions summarized in Figure 2 and the precisions provided with each archived SAGE II NO₂ profile. Figures 2 and 3 suggest that the actual error profile is a smoothed and somewhat smaller version of the archived error bars. Information on the measurement errors has also been obtained by examining the vertical correlation behavior of the profiles and the effect of vertical averaging on the NO₂ variances at individual altitudes during the selected quiescent periods. Table 2 indicates that the measurement error correlation distance (defined as the vertical separation at which the correlation is e^{-1}) is roughly 3–5 km between 25 and 36 km altitude and more than 10 km above this altitude. This correlation structure of the measurement errors for NO₂ as well as the similar structure calculated for the ozone profiles [Cunnold *et al.*, 1990] have been simulated by a

correlation structure of the radiance measurement errors consisting of a decrease to a small value at approximately 0.5 km tangent altitude separation and a correlation which remains roughly constant at a value of approximately 0.3 at all larger separations. Our simulations of the effects of these errors on the retrieved profiles were based upon calculations which included the smoothing introduced by the contribution function employed in the retrieval algorithm. This model can account for the profile standard deviations below 36 km altitude which are a factor of approximately 1.5 smaller than the errors reported in Figure 2 and on the data tapes. This noise model also indicates that because of correlation the effect of vertical averaging of the errors over 5 km is to reduce the error variance by approximately a factor of 2 and not a factor of 5 (as was assumed in Figure 2). The gradient discontinuity in the error profile corresponding to the transition from 1 to 5 km smoothing is therefore not evident in the profile standard deviations shown in Figure 3. Above approximately 42 km altitude, when all concentration profiles are smoothed over 5 km, the profile standard deviations are similar to the measurement errors given on the SAGE II data tapes even though the ad hoc procedure used to arrive at those estimates appears to have been incorrect.

In summary, the archived NO₂ profile error bars are conservative estimates of the profile precision at most altitudes, because they do not allow for the vertical correlation structure of the measurement errors or the smoothing of those errors introduced by the retrieval algorithm. These results do not, however, imply that the vertical resolutions of the retrieved NO₂ profiles are not as good as the nominal resolutions of 1 km below approximately 38 km altitude (and 5 km above this altitude), because the retrieval algorithm utilizes a limb scanning contribution function to distribute the profile updates at each altitude. The updates are thus physically realistic based on the measurement procedure, whereas the measurement errors will be smoothed because of a different vertical correlation structure. Because of the lack of resolution and the large and correlated error bars above 38 km altitude, we consider there to be only a single piece of information in individual NO₂ profiles above 38 km altitude.

The repeatability of measured NO₂ profiles will be affected by a reference height uncertainty for each profile of approximately 0.2 km. This uncertainty arises from satellite ephemeris errors. Buglia [1988] (also see Cunnold *et al.* [1989]) has pointed out that ephemeris estimates are only updated every 7 days and accordingly that profile reference altitude errors are likely to be correlated over periods of approximately 7 days. Since SAGE II scans a 10° latitude band over a few days just once per month, this means that all the profiles within such a latitude band during the month are likely to possess similar reference altitude errors. Shifting the NO₂ profile vertically by 0.2 km will produce an error of a few percent in the NO₂ concentrations above 30 km altitude in part because of the vertical shift in the profile and in part because of the errors in removing the Rayleigh-scattering effects. It might be possible to detect this error because of its 7 day correlation time, using the SAGE II ozone or aerosol profiles. However, for most NO₂ studies the error is likely to be negligibly small.

The absolute uncertainty in the SAGE II NO₂ measurements is primarily dependent on the uncertainty in the difference between the NO₂ absorption cross sections at

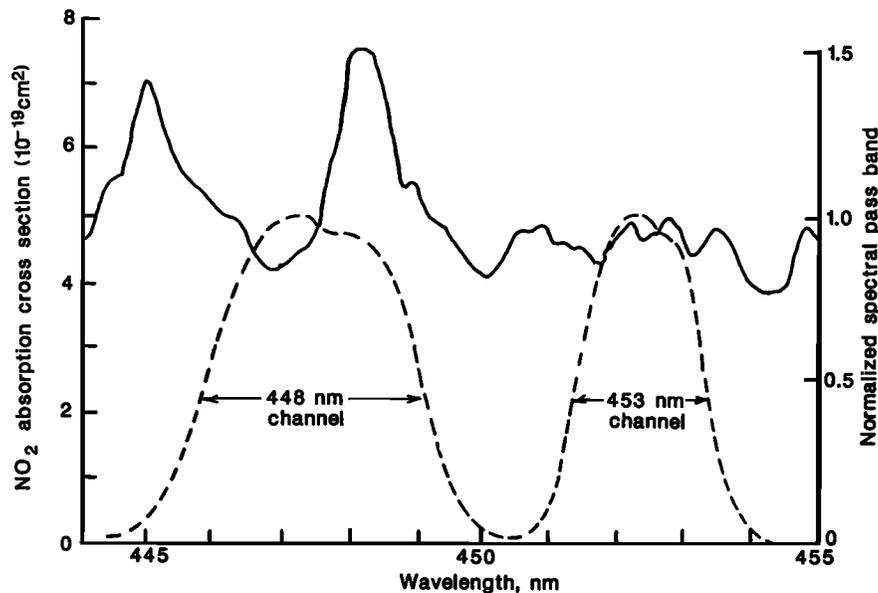


Fig. 4. The absorption cross section of NO₂ over the wavelength range 0.444 to 0.455 μm used in the SAGE II NO₂ retrievals (no temperature dependence is included). Also shown are the bandpass filter functions for SAGE II channels 5 and 6.

0.453 and 0.448 μm . The precise location of these filters and their bandwidths of 0.0020 and 0.0030 μm , respectively, are shown in Figure 4. The SAGE II retrieval is based on absorption coefficients which were measured at 298°K [Goldman *et al.*, 1978]. Measurements of the NO₂ absorption cross section in the vicinity of 0.448 μm at temperatures of 298° and 235°K [Leroy and Rigaud, 1987] and measurements illustrated by Davidson *et al.* [1988] suggest a reduction in the effective absorption cross section in SAGE II channel 6 at typical stratospheric temperatures of approximately 1%. Unfortunately, Leroy and Rigaud's measurements did not extend to 0.4523 μm . However, Davidson *et al.* [1988] indicate that, averaged over the 0.0015- μm bandwidth at 0.453 μm , the absorption coefficient of NO₂ possesses a temperature sensitivity of approximately $\pm 0.5 \times 10^{-22} \text{ cm}^2/\text{°K}$. This sensitivity is in opposite directions at the peaks and valleys of the absorption cross section and is in the sense that the cross-section difference becomes larger at lower temperatures. On the basis of the Davidson *et al.* [1988] data a temperature sensitivity of $-1.5 \times 10^{-22} \text{ cm}^2/\text{°K}$ is estimated for the differential cross section. This translates into an increase in the cross section at typical stratospheric temperatures of approximately $9 \times 10^{-21} \text{ cm}^2$ (12%). Accordingly, the SAGE II NO₂ measurements may overestimate atmospheric NO₂ concentrations by approximately 12%. Moreover, as a result of temperature variations ($\pm 20^\circ\text{K}$) within the 25–40 km measurement region, there may be errors in the NO₂ estimates of $\pm 4\%$.

SAGE II sunrise NO₂ measurements appear to be approximately 30% too large based on both a comparison with atmospheric trace molecules spectroscopy experiment (ATMOS) observations and on an unrealistically small measured sunset to sunrise NO₂ ratio. The problem has been tentatively identified as a solar heating transient in the SAGE II instrument. During sunset the aperture is opened at a tangent altitude of approximately 120 km, a transient occurs as the instrument heats up, but equilibration is complete by the time the scan has reached a tangent altitude of 100 km. At

sunrise, on the other hand, the instrument heats more slowly because the sunlight is attenuated by the low-altitude atmosphere with the result that anomalous signals are measured in the narrow-band NO₂ channels over most of the stratosphere.

This instrumental behavior is confirmed during special events which sometimes occur when satellite sunrises and sunsets occur at extremes of latitudes. At these times, spacecraft sunrise can correspond to ground sunset (and vice versa). These events occur in June and December (see Figure 1) just prior to and just following completely sunlit orbits. The ground sunset (spacecraft sunrise) NO₂ values are found to be 5–10% smaller than normal ground sunset (spacecraft sunset) values, and the ground sunrise (spacecraft sunset) values are approximately 5–10% larger than the typical SAGE II ground sunrise (spacecraft sunrise) values at this latitude. This indicates that during these events the thermal shock produces a 5–10% reduction in the measured NO₂ concentrations during spacecraft sunrise. During these periods the spacecraft barely dips below the horizon and the cooling of the instrument is less than normal; the resulting changes in the signals are therefore smaller than they would be under more typical sunrise conditions. Attempts have been made to adjust the signals for this thermal shock using continuously monitored electronics data. Although the NO₂ sunrise profiles have been significantly improved, it is unclear how to adjust for all the factors which might impact the instrument response. This problem impacts only the narrowest-band channels (i.e., the NO₂ channels). This conclusion is reinforced by studies of the "pitch-180" data taken when the spacecraft is inverted. This is an instrument test configuration in which the instrument looks directly at the Sun from space. At these times the scan mirror is tested for angular dependency by scanning across the Sun; the scan mirror motions simulate both sunrise and sunset events. A transient signal is observed in the SAGE II output as the instrument heats up in response to observing the Sun; however, the response is found to be independent of the scan

mirror position, indicating that the slower transient response in a normal sunrise event results from the absorption and scattering of sunlight by the atmosphere. Again, only the two narrow-band NO₂ channels are affected. There are no plans currently for archiving the NO₂ sunrise data.

Since the SAGE II NO₂ measurements are derived from the two spectral channels utilizing interference filters for passband determination, there could be additional uncertainties on the retrieved NO₂ associated with the degradation of the interference filter with time. Since the designed operational lifetime of the instrument was 2 years, no special calibration scheme was implemented to monitor the changes in the filter bandpass characteristics. The unattenuated solar maximum output from the 0.448- μm channel shows an increase of roughly 17% over a 5-year period, suggesting that the bandwidth is increasing and/or the band center is moving to longer wavelength (or both). Assuming the bandwidth has increased by the exact amount necessary to produce the observed increase in solar output without any shift in the central wavelength, we estimate that the NO₂ cross section in the 0.448- μm channel would have decreased by approximately 2%. This would have resulted in a decrease in the differential cross section of 10%, and underestimation of the NO₂ density by 10% at the end of the 5-year period. If the broadening of the passband has been accompanied by a small shift in the center wavelength of up to 0.005 μm , there could be an additional modulation of 5% on the retrieved NO₂ density depending on the direction of the shift based on the observed shape of the solar spectrum, a larger shift than this is considered unlikely. The 0.453- μm channel is located in a relatively flat NO₂ absorption spectral region and is insensitive to either a broadening of the passband or a shift in center wavelength; moreover, the 448-nm channel is the only SAGE II channel which has undergone a significant change in its throughput over time. The above error estimate from the aging effect of the interference filters is preliminary and is still being evaluated based on a longer time series of engineering data from the instrument.

4. TWO BALLOON INTERCOMPARISONS AT SUNSET

4.1. April 1985 Experiment

Two Centre National de Recherche Spatiale (CNRS) balloon instruments were flown on the same gondola: The first instrument was a scanning spectrometer (spectral range 430–450 nm with resolution 0.2 nm and a measurement frequency equal to one 400-point spectrum per minute), which has already been described by Roscoe *et al.* [1990]. The second was a fixed grating instrument which used a diode array detector. This instrument was made of a commercial Jobin-Yvon spectrometer UFS 200 equipped with an holographic grating of 200 grooves/mm and aperture $F/3$. The detector was a Reticon 512 silicon photodiode array. An entrance slit of 25 μm provided a resolution of 1 nm over the 200–500 nm spectral range. Two four-position wheels in front of the spectrometer provided neutral density filters for adjusting the incoming light flux and a shutter for dark current measurements. The spectrometer was run automatically by an RCA 1802 microprocessor. Spectra transmitted to the ground every minute consisted of 100-ms measurements from the 512 elements. The gondola was Sun-oriented

at $\pm 1^\circ$, and each spectrometer had its own heliostat. The accuracy of the Sun tracking was ± 1 min of arc in both elevation and azimuth.

NO₂ was computed differentially by ratioing the observed and a control spectrum recorded using high Sun at float altitude at the beginning of the flight. The large bandpass signal due to Rayleigh and aerosol scattering was removed by filtering. After correction for ozone absorption the residual spectrum was least squares correlated with an NO₂ absorption spectrum recorded using a calibration cell at the ground prior to the flight. The amount of NO₂ inside the cell was determined by comparison with absorption cross sections measured at laboratory temperature by H. S. Johnston (unpublished data, 1977). The temperature dependence of the NO₂ absorption cross section was ignored in this experiment. Atmospheric NO₂ concentrations were retrieved in 2-km-thick layers by an onion-peeling method. The rms error calculated for each spectrum was included in the retrieval procedure. The absolute calibration error was estimated to be $\pm 8\%$. For more details on the data analysis procedure and a discussion of precision and accuracy, see Roscoe *et al.* [1990], Pommereau *et al.* [1987].

This flight took place at the Centre National d'Etudes Spatiales (CNES) balloon range at Aire sur l'Adour on April 20, 1985. Lift off occurred at 1413 UT (local noon was at 1245 UT), the balloon reached float altitude around 6.2 mbar (approximately 34.3 km) 1.5 hours later and began drifting toward the northeast. Sunset (solar zenith angle (SZA) = 90°), occurred at 1842 at 44°31'N, 00°58'E at a level of 7.3 mbar (approximately 33.15 km) and loss of Sun (SZA = 95.2°) was at 1913 at 44°40'N, 01°08'E at the same altitude. The Sun was lost on the scanning spectrometer at a tangent height of 10 km. A wrong command order made the fixed grating instrument stop at 13.5 km.

The precision of the fixed spectrometer was better than that of the scanning one because the fixed spectrometer was less sensitive to light fluctuations due to scintillation and aerosol layering. The two profiles however agreed within their rms errors, and since their systematic errors are the same, a weighted average is used for the comparison with the SAGE II measurements. This average profile is referred to as "balloon data."

Figure 5 shows the location of the balloon on April 20 at sunset and the tangent point observed at SZA = 90° together with the three SAGE II sunset events on April 21, 22, and 23. Since the measurements were not made on the same day a trajectory analysis is required for the intercomparison. During the 3 days following the balloon flight the wind was blowing from the southwest at a speed between 15 and 20 knots above 26 km, from the east at 5 knots or less, between 20 and 24 km, and from the southwest again, between 16 to 20 km. The trajectories of the air masses observed from the balloon at several altitudes on April 20 at sunset have been reconstructed for the 3 following days based upon radiosonde data at Bordeaux. Table 3 shows the distances between these trajectories and the SAGE II tangent points at the time of each event. The best comparison should be with the satellite observations of April 21. On April 22 the comparison should be restricted to levels below 25 km, while the data of April 23 should not be compared, since not only is the temporal separation 3 days, but the distances are 1000 km or more (except around 24 km).

The NO₂ vertical distributions observed from the balloon

SAGE II MEASUREMENT LOCATIONS

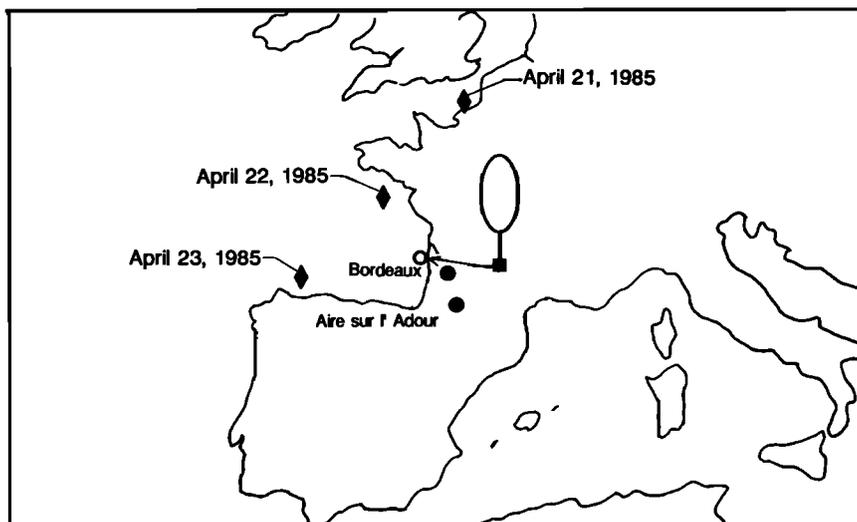


Fig. 5. Location of the balloon on April 20 at sunset with tangent point at 20 km (arrow). The three SAGE II events to which the data could be compared are indicated by squares in which the date has been included. Although the latitude of the balloon and the satellite tangent point on April 23 is the same, the air mass observed from the balloon 3 days earlier is too far to the northeast to make the comparison significant. The best comparison is obtained with data of April 21.

on April 20 and from the satellite on April 21 and 22 are shown on Figure 6. Within the uncertainty of SAGE II, the satellite data agrees with the balloon observations on both days below 25 km but agree above 25 km only on April 21. Therefore provided the comparison is restricted to distances closer than 1000 km, there is no significant difference between the two sets of data. The relative difference, (SAGE II-Balloon)/Balloon, are displayed on Figure 6 together with SAGE II and balloon uncertainties. On the average above 22 km on April 21 the SAGE II concentrations are larger than the balloon ones by 1.1% with a standard deviation of $\pm 3.9\%$.

4.2. September 1985 Experiment

Three instruments were flown in this experiment: the CNRS diode array spectrometer used in April, and two scanning instruments one of which was built by the University of Tokyo (resolution 0.15 nm, spectral range 435–450 nm). The balloon flight took place at Aire sur l'Adour on September 19 as part of the global budget of stratospheric trace constituents (GLOBUS) NO_x campaign. Lift off oc-

curred in the early afternoon and float altitude was reached around 32 km, 3 hours before sunset (SZA = 90°). The sunset was observed at 1850 UT from an altitude of 32.1 km at 43°45'N, 1°17'E. The measurements were made until the Sun was lost at tangent height of 4.5 km by the last instrument.

The results of these simultaneous observations and the analysis and calibration procedures have been carefully intercompared. It appears that the largest remaining uncertainty in these stratospheric NO₂ measurements is associated with the temperature dependence of the NO₂ absorption cross section. Using, for example, the laboratory data of *Leroy and Rigaud* [1987], a reduction of the temperature from 298° to 235°K implied a concentration reduction of 12%. This factor is exactly the one required to put the balloon intercomparison campaign (BIC) visible and infrared measurements in agreement [*Roscoe et al.*, 1988]. A weighted average NO₂ profile is again obtained from the three independent data sets. In this case it has been corrected for the NO₂ temperature dependence and interferences.

Figure 7 shows the location of the balloon on September 19 at sunset and the closest SAGE II events a few days earlier on September 14, 15, 16, and 17. The wind was light and blowing from the south in the upper troposphere and the lower stratosphere but from the west-southwest at 15 to 20 knots above 25 km. Therefore the satellite measurements on September 14 and 15 are too far in advance to make useful comparisons. A trajectory analysis has been conducted as for April. The distances between the locations of the air mass observed from the balloon on September 19 at the time of the SAGE events are reported in Table 4. At all levels the closest distance is for the satellite observations of September 17.

Figure 8 shows the comparison of the NO₂ profiles measured by SAGE II on September 16 and 17. From one day to

TABLE 3. Distances Between SAGE II Sunset Profiles Measured Near Aire sur l'Adour in April 1985 and the Back Trajectories at Several Altitudes of the Air Masses Observed by the Balloon

Altitude, km	Day		
	April 21	April 22	April 23
32	400	1500	2200
28	0	1100	2000
24	700	300	200
20	350	350	1000
16	350	700	1300
12	200	700	1200

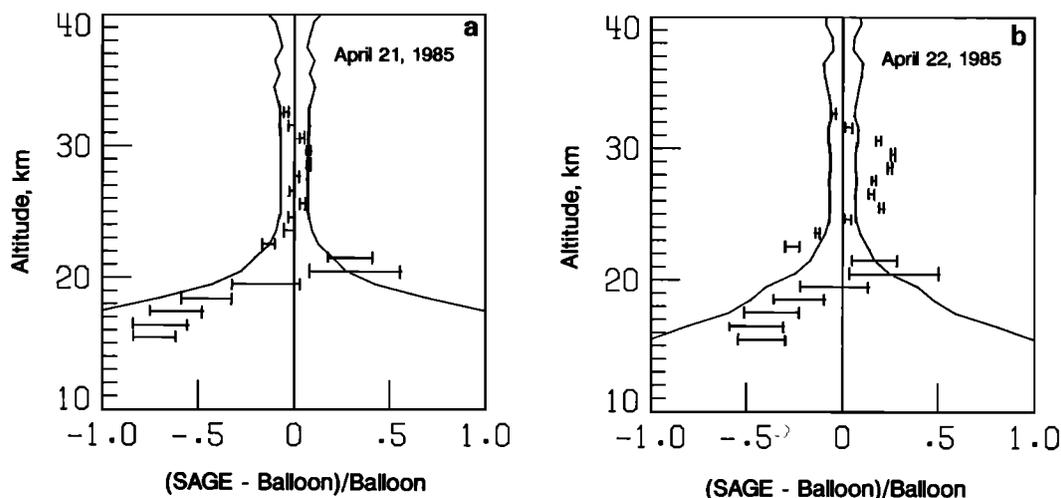


Fig. 6. Relative difference between balloon and satellite observations of NO₂ reported in the SAGE II uncertainty envelope. The error bars show the balloon data RMS errors. (a) April 21, 1985; (b) April 22, 1985.

the next the concentration decreased at all altitudes between 20 and 30 km. On September 17 the balloon and the satellite profiles agree within the error bars. The relative difference defined as $(\text{SAGE} - \text{Balloon})/\text{Balloon}$ is shown on Figure 8. There is some structure on the SAGE II data which is not in evidence in the balloon results. On the average in the stratosphere above 22 km, the difference is found to be approximately $-2\% \pm 7\%$ with the balloon concentrations being smaller.

4.3. Summary of Balloon Intercomparison

These two comparisons indicate that there is no systematic bias between the balloon and SAGE II NO₂ measurements. In the stratosphere, when the two air masses observed are closer than 1000 km, the differences do not exceed -9% and $+5\%$. The comparison begins to degrade at

22 km. Although these numbers result from two comparisons involving five independent profiles, the large changes of NO₂ concentrations observed from one day to the other by SAGE II, allow the possibility that this excellent agreement is fortuitous. Moreover, it should be noted that the September data are corrected for NO₂ absorption cross-sections temperature dependence and interferences, while the April data are not (a difference of approximately 12%). Accordingly, we stress only that the agreement is within 20% at all altitudes above 22 km. The absolute calibration uncertainty of the balloon data is estimated to be $\pm 8\%$ and the agreement with infrared occultation measurements performed during BIC after correcting the visible data for temperature, indicates that a larger error is unlikely.

The last source of uncertainty specific to occultation techniques is that NO₂ is undergoing photochemical change

SAGE II MEASUREMENT LOCATIONS

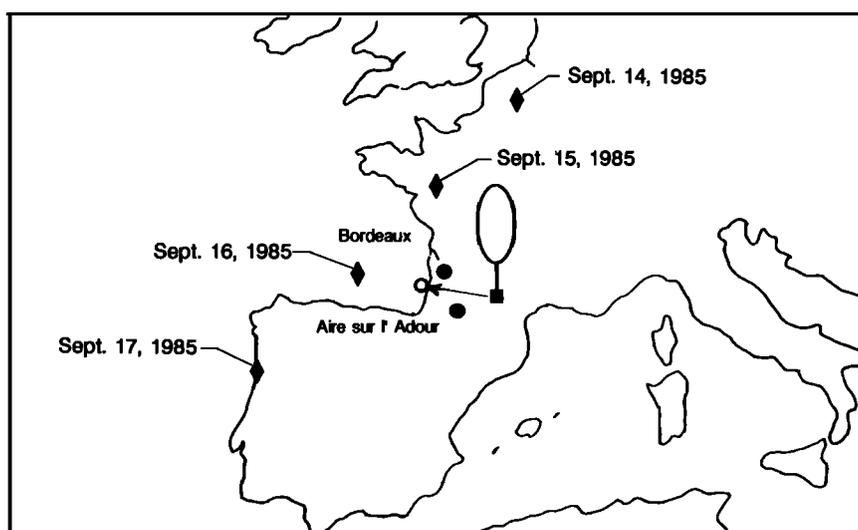


Fig. 7. Same as Figure 5 but for September 1985. The balloon was launched on September 19. The closest SAGE II observations were made on September 17.

TABLE 4. Distances Between SAGE II Sunset Profiles Measured Near Aire sur l'Adour in September 1985 and the Back Trajectories at Several Altitudes of the Air Masses Observed by the Balloon

Altitude, km	Day	
	September 16	September 17
30	2300	680
25	1000	220
20	1200	500
15	280	180

during the sunset period. According to *Roscoe and Pyle* [1987], this will result in an overestimation of the NO₂ concentration at sunset by 2% at 31.5 km, 10% at 25 km, and 18% at 18 km. The correction is different for orbiting and balloon-borne platforms. No satisfactory code for correcting this effect exists at the moment.

5. COMPARISON WITH ATMOS MEASUREMENTS

The ATMOS experiment was flown aboard SPACELAB 3 and made solar occultation measurements using an interferometer operating between 2 and 15 μm . Ten sunset profiles of NO₂ were recorded at 25–33°N on April 30/May 1, 1985. *Russell et al.* [1988] report a weighted average of 7 of those profiles located between 268.4°E and 69.4°E longitude and 32.2°N and 25.6°N. SAGE II made similar measurements at this location on April 26/27 (i.e., 4 days earlier). The SAGE II measurements on these days exhibited longitudinal variations of less than approximately 4% in NO₂ in planetary waves 1–4 (which is comparable with below the measurement noise level at 5–10 mbar) and of approximately 1% in temperature. Therefore a comparison is made of the weighted average NO₂ ATMOS profile reported by *Russell et al.* [1988] against the SAGE II zonally averaged sunset profile located closest to 29°N on April 27 (Figure 9). In this comparison, neither ATMOS nor SAGE II profiles have been corrected for the temporal variation of NO₂ during sunset. The effect of that correction would be to reduce the retrieved profiles by approximately 2% [*Russell et al.*, 1988]. The agreement between the profiles is excellent at the NO₂

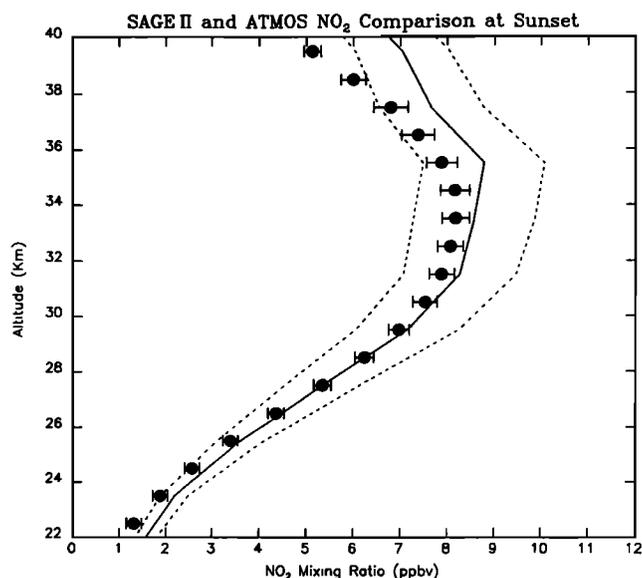


Fig. 9. Comparison between SAGE II sunset NO₂ zonal average (dots) at 29°N for April 26/27, 1985, and ATMOS measurements on April 30/May 1 averaged over 268.0°E to 69.4°E longitude. The standard deviation of the 15 profiles comprising the SAGE II zonal average is indicated by the error bars. The range of uncertainty associated with the ATMOS measurements is indicated by the pair of dotted lines.

mixing ratio maximum. Below 25 km altitude where the SAGE II profiles are less precisely measured (and aerosol contamination is possible) the agreement is satisfactory.

There appears to be a systematic difference between the ATMOS NO₂ measurements and the SAGE II profiles above 36 km, with the SAGE II concentrations being 10–15% less than those for ATMOS at 40 km, and the scale height of NO₂ for SAGE II being less than for the ATMOS measurements. While the respective error bars of the two measurements do overlap, the difference is still significant in terms of its effect on the NO_x budget of the upper stratosphere. The climatology of the SAGE II NO₂ measurements has been studied by J. M. Zawodny with the aid of a photochemical model for the partitioning of the NO_x (NO_x = NO + NO₂ + NO₃ + 2 ×

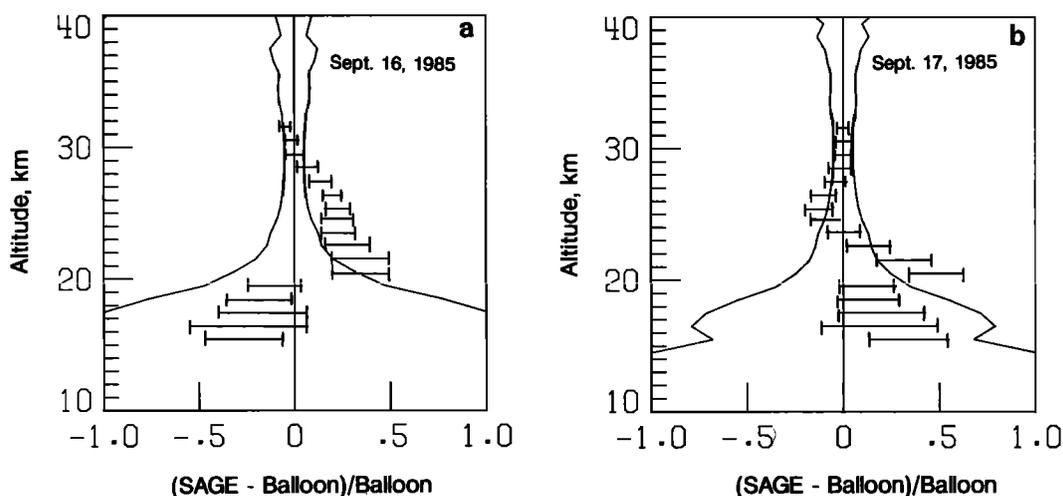


Fig. 8. Same as Figure 6 but for September 1985. (a) September 16, 1985; (b) September 17, 1985.

N₂O₅) family. One result from this study is that the NO_x inferred from the SAGE II NO₂ measurements agreed well with the results for most two-dimensional models in the lower and midstratosphere. The SAGE II derived NO_x peaked at 36 km versus a peak at 40 km calculated in the models. The quantitative details of this difference in NO_x is very similar to the difference between the SAGE II and ATMOS profiles. While the modeling of twilight observations is not easy, the model being used should not suddenly change behavior above 36 km. The possible causes for these apparent differences above 36 km altitude are being investigated; it should, however, be noted that this is a region where the SAGE II profiles are being vertically smoothed over 5 km, and there is not much information in the profiles.

6. COLUMN NO₂ COMPARISON

Routine measurements of the twilight column abundance of NO₂ have been made at Lauder, New Zealand, since late 1980 and have been discussed in the literature [McKenzie and Johnston, 1982; Johnston and McKenzie, 1989]. Lauder is located at 45°S, which is a latitude at which SAGE II samples frequently. However, there are difficulties in performing an intercomparison: first, the ground-based instruments measure only the sunlit half of a slant column, and second, the accuracy and precision of the SAGE II measurements begin to decrease significantly below approximately 25 km altitude at mid-latitudes. The Lauder measurements can be converted to vertical columns although this process introduces a number of uncertainties [Johnston and McKenzie, 1989]. In the comparison reported here a weighting factor of 20 for the conversion between vertical columns and slant path columns has been used. This factor is profile shape dependent and may be in error by up to 20% [Solomon *et al.*, 1987]. Lauder columns are usually considered to be representative of the column above 15 km altitude. Since, however, we have chosen to integrate the SAGE II columns down to only 20 km altitude (because of measurement and retrieval uncertainties), we have reduced the inferred Lauder vertical columns by multiplying by a factor of 0.8 to account for the different column base altitudes.

The comparison between SAGE II columns above 20 km altitude and the adjusted Lauder columns is shown in Figure 10. For a latitudinal coincidence criterion of ±5° there are 1–5 days of SAGE II observations associated with an individual traverse through this latitude band (see Figure 1). SAGE II zonal means for individual days are included in Figure 10; the squares represent zonal means for a ±2.5° coincidence criterion, corresponding to which there will be 1–2 days in an individual traverse. Excellent agreement between the annual cycles in the SAGE II and Lauder NO₂ columns is evident. The average difference between the adjusted Lauder and SAGE II columns is $1 \pm 2.5 \times 10^{14}$ cm⁻²; however, the SAGE II data shows a long-term decrease in NO₂ which is not shown in the Lauder data; the reason for this difference is unknown [see McKenzie *et al.*, 1989], but the long-term changes in the output of the 0.448-μm filter, which were previously mentioned, may be contributing to this difference.

7. COMPARISONS AGAINST LIMS MEASUREMENTS

SAGE II NO₂ measurements may be compared against limb infrared monitor of the stratosphere (LIMS) measure-

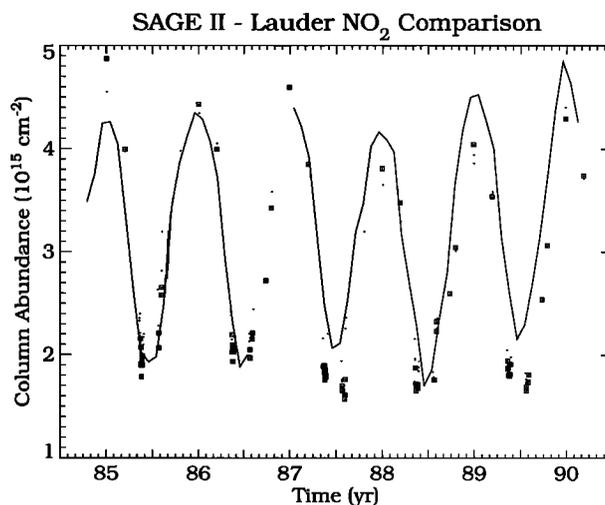


Fig. 10. Comparison between the scaled (see text) monthly averaged Lauder (45°S) column measurements (line) at sunset and the zonally averaged SAGE II column abundances above 20 km altitude. SAGE II zonal averages between 42.5° and 47.5°S are indicated by boxes; zonal averages between 40° and 50°S are indicated by dots.

ments made in 1978/1979. This comparison is made at tropical latitudes. Months between November and May are selected in each of which SAGE II provided several days of observations in the tropics in 1984/1985. Figure 11a shows the comparison of the mean SAGE II mixing ratios at sunset during November, January, March and May in the 5°–15°N and 5°–15°S latitude bands against LIMS daytime observations in similar months and at the same latitudes [Russell, 1986]. The standard deviations of the eight monthly/latitude belt means are also indicated. The SAGE II standard deviations are larger at most pressure levels, because there are just a few days of data forming each of these means. The comparison is only useful when the profiles are adjusted for the time difference between the two sets of observations (the LIMS observations were made at approximately 1400 LT). The photochemical model employed earlier incorporating values of the photodissociation rate of NO₂ from Madronich *et al.* [1985] was used to adjust LIMS values to sunset. The adjustment factor used is slightly altitude dependent and is between 1.5 and 1.6. The difference (LIMS-SAGE II)/SAGE II after this adjustment is shown in Figure 11b. LIMS values are approximately 20% larger than SAGE II between 15 and 3 mbar where the LIMS experiment accuracy is approximately 20% [Russell *et al.*, 1984]. The differences become much greater at altitudes lower than 15 mbar where the potential inaccuracy of the LIMS observations increases rapidly with decreasing altitude because of molecular oxygen interference [Russell *et al.*, 1984]. It should be noted that the SAGE II analysis by J. M. Zawodny show evidence of a quasi-biennial oscillation in NO₂ with a magnitude of approximately 10%, and early 1979 is the beginning of the easterly phase, whereas early 1985 is the beginning of the westerly phase.

8. SAGE I/II COMPARISON

Figure 12 shows a comparison between SAGE I and II tropical sunset profiles of NO₂ in the tropics and at mid-

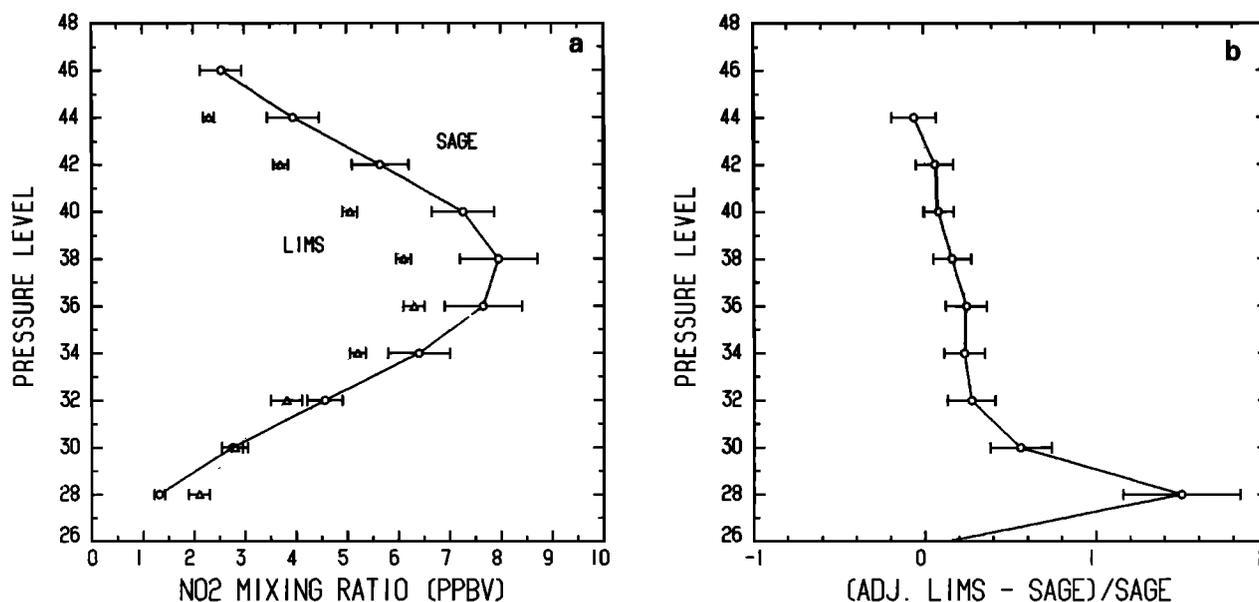


Fig. 11. (a) Comparison between averaged LIMS daytime NO₂ mixing ratios 5°–15°N and 5°–15°S in November 1978 and January, March, and May 1979 and SAGE II sunset observations in these latitude bands in November 1984 and January, March, and May 1985. Standard deviations of the monthly mean values are indicated by the horizontal lines. (b) The ratio (LIMS-SAGE)/SAGE obtained after the LIMS mixing ratios have been adjusted for the local time difference between the measurements using a photochemical model. (See Table 2 for example for the conversion between pressure levels and atmospheric pressures).

latitudes. Following an extensive analysis of the SAGE I data for trends in stratospheric ozone, the originally archived SAGE I NO₂ (and other species) observations [Chu and McCormick, 1986] have been revised. The revised data set was archived in the NSSDC in 1990. The differences between the SAGE I profiles are the result of errors in the tropical temperature profiles used in the retrievals of the first version of the SAGE I data and a change in the procedure for establishing the reference heights of the profiles (see discussion by Cunnold *et al.* [1989]). A comparison of the revised SAGE I profile against the SAGE II profile would seem to suggest some changes in stratospheric NO₂ during the 1980s and a different profile shape.

It is important, however, to note that the SAGE I and SAGE II measurements utilize different techniques for inferring NO₂. The SAGE I NO₂ retrievals are based to a large extent on the extinction at 0.385 μm . This means that SAGE I NO₂ retrievals are particularly sensitive to the separation of the Rayleigh and NO₂ contributions. Measurement noise and difficulties associated with removing the Rayleigh, ozone, and aerosol contributions lead to a precision of 15–20% for SAGE I profiles (Chu and McCormick [1986] give equivalent random errors of $5 \times 10^8 \text{ cm}^{-3}$ for NO₂ concentrations at 30 km altitude and $2 \times 10^8 \text{ cm}^{-3}$ at 40 km altitude). This precision occurs following smoothing of the profiles over 3 km at all altitudes during the retrieval procedure. In contrast to SAGE II, strong positive correlations are found between SAGE I ozone and NO₂ variations in quiescent conditions. This is probably the result of correlated measurement errors at 0.45 and 0.60 μm , which have a much larger effect on the NO₂ profiles than on the ozone profiles. Measurement errors for SAGE I NO₂ profiles are calculated to have a correlation distance of approximately 7 km. The largeness of the SAGE I error bars suggests that there are no more than two pieces of independent information in individual SAGE I NO₂ profiles.

The differences in the median profiles shown in Figure 12 may result in part from the previously discussed temperature sensitivity of the NO₂ (differential) cross-section which may be producing a 12% overestimate of the SAGE II concentrations. The quoted accuracy of 16% for SAGE I observations is unrelated to this possible bias in the SAGE II observations. The Rayleigh-scattering contribution is less certain for the SAGE I observations and as already mentioned, the SAGE I NO₂ observations are much more sensitive to any uncertainty in this term. Moreover, the altitude registration procedure is less precise for SAGE I and the quoted uncertainty in reference altitude of 0.25 km [Buglia, 1989] must be also considered as a potential bias. For example, an increase of 0.8% in the center frequency of the 0.385- μm (nominal) filter would result in an increase of NO₂ concentrations both because of a reduction in the Rayleigh extinction and because this would imply downward shifts of approximately 0.2 km in the reference altitudes. This would lead to an increase in SAGE I NO₂ concentrations above the NO₂ concentration peak by approximately 40% together with a significant reduction in the NO₂ scale height. The peak concentration would increase approximately 10% and would rise slightly in altitude. Below 27 km, where SAGE I concentrations are quite inaccurate because of uncertainties in both Rayleigh and aerosol contributions, there would be a decrease in the NO₂ concentrations. Because of this uncertainty in the Rayleigh-scattering contribution to the SAGE I NO₂ profiles, we would not wish to infer any trend in atmospheric NO₂ from the differences between the SAGE I and SAGE II NO₂ profiles.

9. CONCLUSIONS

SAGE II NO₂ profiles are derived from the difference between the radiation received at 0.448 μm and at 0.453 μm (i.e. by a differential technique). The bandwidth of the filters

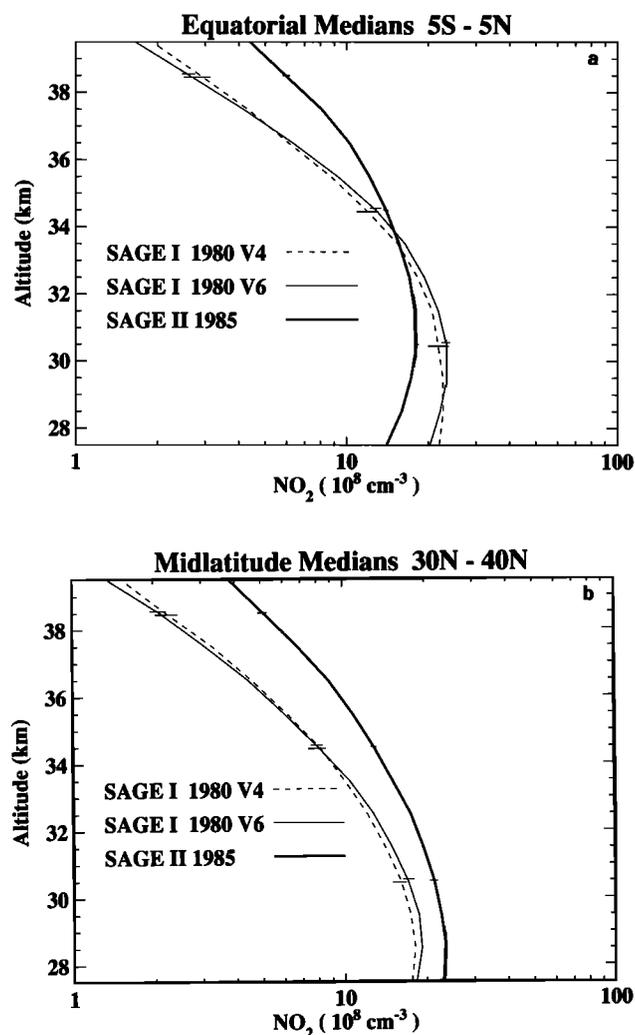


Fig. 12. The figure shows median NO₂ concentration profiles derived from the originally archived (version 4) and reprocessed (version 6) SAGE I sunset data, as well as the SAGE II sunset profile data over a one year period for the latitude bands (a) 5°S to 5°N and (b) 35°N to 45°N. In Figure 12a the SAGE I sampling represents six passes through the equator (April, June, August, September, October, and November of 1980) with 82 profiles available in the original data set, and 98 profiles available from the reprocessed data set. The SAGE II sampling represents six equatorial passes (March, May, July, August, September, and November of 1985) with 125 profiles. In Figure 12b the SAGE I sampling represents eight passes through 35°N with 193 profiles available in the original data set, and 251 profiles available from the reprocessed data set. The SAGE II sampling represents seven passes through 35°N with 348 profiles. The horizontal bars on each curve represent the 95% confidence interval on the median of the measurements.

are 0.003 and 0.002 μm respectively. The measurement technique is self-calibrating in that the Sun scan begins "above the atmosphere," at a tangent altitude of 120 km, immediately prior to each sunset occultation. After acquiring the Sun the instrument scans back and forth across it as it is occulted by the atmosphere. Each individual profile altitude is thus scanned approximately 6 times. This procedure results directly in an estimate of the precision of each NO₂ profile resulting from measurement noise provided that the correlation structure of the measurement errors as a function of tangent altitude is known. The NO₂ sunset profiles and accompanying precision estimates (based on ad hoc assump-

tions about the noise correlation) are being archived at the National Space Science Data center (NSSDC).

The precision of the NO₂ profiles is determined principally by the measurement noise but below 30 km altitude substantial contributions arise from uncertainties in the concentrations of molecular scatterers and aerosol particles. The variances of the measured profiles during atmospherically quiescent periods indicate that the error bars archived with the profiles provide conservative estimates of the random profile measurement errors by a factor of approximately 1.5 at altitudes below approximately 38 km. These variances indicate that the precision of the sunset profiles is approximately 5% between 36 km altitude and a latitude-dependent lower altitude at which the NO₂ mixing ratio equals approximately 4 ppbv (approximately 25 km in the tropics and 29 km at mid-latitudes). At lower altitudes, the precision of the measurements is roughly 0.2 ppbv. At altitudes above 36 km the precision is indicated to worsen by approximately 3% per kilometer increase in height. The noise correlation distance which reflects the effect of smoothing of the measurement noise during the retrieval changes from 3 to 5 km below the transition from 5 to 1 km smoothing to more than 10 km above it. These correlations can account for the differences between the observed profile standard deviations and the archived error bars and for the absence of a sharp change in the precision of the profiles at the transition altitude. Because of the large error bars and vertical smoothing of the profiles at high altitudes, there is likely to be only a single piece of information in the individual SAGE II NO₂ profiles above approximately 38 km altitude.

The accuracy of the sunset NO₂ profiles is estimated to be approximately 15% primarily because of uncertainties in the temperature dependence of the NO₂ absorption cross sections. The SAGE II profiles are based on cross sections measured at 298°K; the temperature sensitivities reported by Davidson *et al.* [1988] would suggest that the SAGE II concentrations are approximately 12% too large. Long-term changes in the output of the 0.448- μm filter may have introduced a decrease in the reported NO₂ concentrations of approximately 10% between 1984 and 1989.

The SAGE II sunrise NO₂ profiles are unreliable, because it has not been possible to remove a solar heating transient affecting only sunrise NO₂ measurements. Currently, there are no plans to archive these profiles.

The NO₂ profiles have been compared against almost coincident balloon-measured profiles over Southern France. On both occasions, agreement within approximately 10% was obtained between 23 and 32 km altitude (the highest altitude of the balloon observations). Zonally averaged vertically integrated profiles exhibit a similar seasonal variation to column measurements at Lauder, New Zealand. Zonally averaged SAGE II NO₂ profiles have also been compared against ATMOS profiles obtained 4 days later. Agreement within approximately 10% was found between 23 km and 37 km altitude. Above 37 km altitude the SAGE II profiles decrease rapidly with increasing altitude and diverge from the ATMOS profiles. This decrease in the SAGE II profiles is under investigation. These intercomparisons suggest that the SAGE II NO₂ profiles are valid over at least the 23 to 37 km altitude range at mid-latitudes.

On the basis of a one-dimensional model of the diurnal variation of NO₂ the SAGE II NO₂ profiles in 1985 are approximately 20% smaller than LIMS measurements in the

tropics in 1979 between 3 and 15 mbar. Comparisons have also been made against SAGE I profiles. These profiles were revised in 1990 as a result of changes in the procedure for arriving at the reference altitudes of the profiles. Even with 3-km profile smoothing the precision of the SAGE I NO₂ profiles is approximately three times worse than for the SAGE II profiles and no more than two independent NO₂ measurements are therefore to be expected in an individual SAGE I NO₂ profile. The median SAGE I profiles exhibit smaller NO₂ concentrations than SAGE II profiles above 34 km altitude and have a smaller NO₂ scale height. Below the NO₂ concentration maximum, relative to the SAGE II profiles, the SAGE I NO₂ concentrations are smaller at mid-latitudes and larger in the tropics. The SAGE I and SAGE II NO₂ measurement techniques are, however, different and each have estimated accuracies of approximately 15%. Moreover, the SAGE I measurements are extremely sensitive to the accurate removal of Rayleigh-scattering effects. Therefore we do not interpret differences between the SAGE I and SAGE II NO₂ measurements as indicative of changes in atmospheric NO₂ between 1980 and 1985.

Acknowledgments. We thank R. L. McKenzie for his data on NO₂ column variations at Lauder, New Zealand. This research was supported in part by NASA contracts NAS1-18487 and NAS1-18938 (D. Cunnold), NAS1-18460 (R. Veiga), and NAS1-18306 (D. Murcray).

REFERENCES

- Buglia, J. J., Effects of ephemeris errors on the accuracy of the computation of the tangent point altitude of a solar scanning ray as measured by the SAGE I-II instrument, *NASA Tech. Publ.*, 2866, 1989.
- Chu, W. P., Inversion technique for SAGE II data, in *RSRM 87: Advances in Remote Sensing Retrieval Methods*, edited by A. Deepak, H. E. Fleming, and J. S. Theon, pp. 243–252, A Deepak, Hampton, Va., 1989.
- Chu, W. P., and M. P. McCormick, SAGE observations of stratospheric nitrogen dioxide, *J. Geophys. Res.*, 91, 5465–5476, 1986.
- Chu, W. P., M. P. McCormick, J. Lenoble, C. Brogniez, and P. Prevost, SAGE II inversion algorithm, *J. Geophys. Res.*, 94, 8339–8352, 1989.
- Cunnold, D. M., W. P. Chu, R. A. Barnes, M. P. McCormick, and R. E. Veiga, Validation of SAGE II ozone measurements, *J. Geophys. Res.*, 94, 8447–8460, 1989.
- Davidson, J. A., C. A. Cantrell, A. H. McDaniel, R. E. Shetter, S. Madronich, and J. G. Calvert, Visible-ultraviolet absorption cross-sections for NO₂ as a function of temperature, *J. Geophys. Res.*, 93, 7105–7112, 1988.
- Goldman, A., F. G. Fernald, W. J. Williams, and D. G. Murcray, Vertical distribution of NO₂ in the stratosphere as determined from balloon measurements of solar spectra in the 4500 Å region, *Geophys. Res. Lett.*, 5, 257, 1978.
- Johnston, P. V., and R. L. McKenzie, NO₂ observations at 45°S during the decreasing phase of solar cycle 21, *J. Geophys. Res.*, 94, 3473–3486, 1988.
- Leroy, B., and P. Rigaud, Visible absorption cross-sections of NO₂ at 298 K and 235 K, *Ann. Geophys.*, 5a(4), 247–250, 1987.
- Madronich, S., D. R. Hastic, H. I. Schiff, and B. A. Ridley, Measurement of the photodissociation coefficient of NO₂ in the atmosphere, II, Stratospheric measurements, *J. Atmos. Chem.*, 3, 233–245, 1985.
- McKenzie, R. L., and P. V. Johnston, Seasonal variations in stratospheric NO₂ at 45°S, *Geophys. Res. Lett.*, 9, 1255–1258, 1982.
- McKenzie, R. L., P. V. Johnston, J. M. Zawodny, and M. P. McCormick, NO₂ column intercomparison between ground-based measurements at Lauder, New Zealand (45°S) and collocated SAGE II satellite measurements, in *Ozone in the Atmosphere*, edited by R. D. Bojkov and P. Fabian, pp. 310–313, A. Deepak, Hampton, Va., 1989.
- Noxon, J. F., Correction (to papers on tropospheric and stratospheric NO₂), *J. Geophys. Res.*, 4560–4561, 1980.
- Noxon, J. F., E. C. Whipple, Jr., and R. S. Hyde, Stratospheric NO₂, I, Observational method and behavior at mid-latitude, *J. Geophys. Res.*, 84, 5047–5065, 1979.
- Pommereau, J. P., et al., Intercomparison of Stratospheric NO₂ and NO₃ measurements during MAP/GLOBUS 1983, *Planet. Space Sci.*, 35, 615–629, 1987.
- Roscoe, H. K., et al., Intercomparison of remote measurements of NO and NO₂, *J. Atmos. Chem.*, 10, 111–144, 1990.
- Roscoe, H. K., and J. A. Pyle, Measurements of solar occultation: The error in a naive retrieval if the constituent concentration changes, *J. Atmos. Chem.*, 5, 323–341, 1987.
- Roscoe, H. K., B. J. Kerridge, L. J. Gray, R. J. Wells, and J. A. Pyle, Simultaneous measurements of stratospheric NO and NO₂ and their comparison with model predictions, *J. Geophys. Res.*, 91, 5405–5420, 1986.
- Russell, J. M. III, Middle atmosphere composition revealed by satellite observations, in *Middle Atmosphere Program Handbook for MAP*, vol. 22, pp. 197–210, University of Illinois, Urbana, 1986.
- Russell, J. M. III, et al., Validation of nitrogen dioxide results measured by the limb infrared monitor of the stratosphere (LIMS) experiment on NIMBUS 7, *J. Geophys. Res.*, 89, 5099–5108, 1984.
- Russell, J. M. III, C. B. Farmer, C. P. Rinsland, R. Zander, L. Froidevaux, G. C. Toon, B. Gao, J. Shaw, and M. Gunson, Measurements of odd nitrogen compounds in the stratosphere by the ATMOS experiment on spacelab 3, *J. Geophys. Res.*, 93, 1718–1736, 1988.
- Russell, P. B., et al., Satellite and correlative measurements of the stratospheric aerosol, II, Comparison of measurements made by SAGE II, dustsondes and an airborne lidar, *J. Atmos. Sci.*, 38, 1295–1312, 1981.
- Solomon, S., A. L. Schmeltekopf, and R. W. Sanders, On the interpretation of zenith sky absorption measurements, *J. Geophys. Res.*, 92, 8311–8319, 1987.
- W. P. Chu, M. P. McCormick, R. E. Veiga, and J. M. Zawodny, NASA Langley Research Center, Hampton, VA 23665.
- D. M. Cunnold, School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332.
- F. Goutail and J. P. Pommereau, Service d'Aéronomie, CNRS, 91371 Verrières le Buisson, France.
- N. Iwagami, Geophysics Research Laboratory, University of Tokyo 113, Japan.
- J. Lenoble, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq., Cedex, Lille, France.
- D. Murcray, Department of Physics, University of Denver, Denver, CO 80208.
- W. Peetermans and P. C. Simon, Institut d'Aéronomie Spatiale, Bruxelles, Belgium.
- K. Shibasaki, Kokugakuin University, Tokyo 150, Japan.

(Received August 30, 1990;
revised May 13, 1991;
accepted May 13, 1991.)