

Measurements of Reactive Nitrogen in the Stratosphere

B. Sen, G.C. Toon, G. El. Osterman, J.-F. Blavier, J.J. Margitan, and R.J. Salawitch
Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

G.K. Yue
NASA Langley Research Center, Hampton, VA

Edit Date: 24.3.1997

Proposed Journal: Journal of Geophysics] Research

Received _____ ; accepted _____

Short title: STRATOSPHERIC NO_y OBSERVATIONS

Abstract.

We present volume mixing ratio profiles of NO, NO₂, HNO₃, HNO₄, N₂O₅, and ClNO₃ and their composite budget (NO_y), from 20 to 39 km, measured remotely in solar occultation by the JPL MkIV Interferometer during a high-altitude balloon flight from Fort Sumner, New Mexico (35°N) on 25 September 1993. In general, observed profiles agree well with values calculated using a photochemical steady state model constrained by simultaneous MkIV observations of long-lived precursors and aerosol surface area from SAGE II. The measured variation of concentrations of NO_x (= NO + NO₂) and N₂O₅ between sunrise and sunset reveals the expected ≈2:1 stoichiometry at all altitudes. Despite relatively good agreement between theory and observation for profiles of NO and HNO₃, the observed concentration of NO₂ becomes progressively higher than model values below 30 km, with the discrepancy reaching 33% at 22 km. Consequently, the observations suggest an incomplete understanding of factors that regulate the NO/NO₂ and NO₂/HNO₃ ratios below 30 km.

Data collected during September 1993 and flights in September 1990 and April 1993 at 35°N reveal a decrease in the NO_x/NO_y ratio for increasing aerosol surface area, following the eruption of Mt. Pinatubo. These observations are consistent with the heterogeneous hydrolysis of N₂O₅ being the dominant sink of NO_x between altitudes of 18 and 24 km for the encountered conditions (e.g., surface area as high as 14 μm²cm⁻³, and temperature from 209 to 219 K).

Introduction

Reactions involving NO and NO₂ constitute the primary process for chemical removal of stratospheric O₃ between altitudes of approximately 24 to 36 km [e.g., Crutzen, 1970; Johnston, 1971]. The abundance of NO, (= NO + NO₂) regulates the concentration of chlorine monoxide (ClO) as well as the ratio of OH to HO₂ in the mid-latitude lower stratosphere for air unaffected by polar stratospheric clouds [e.g., Wennberg *et al.*, 1994]. The partitioning of NO_x relative to N₂O₅ and HNO₃, the dominant reservoirs of the nitrogen oxide family of gases (NO_y, defined as the sum of the concentration of NO_x, HNO₃, HNO₄, 2·N₂O₅, ClNO₃, BrNO₃, NO₃, and HNO₂), is controlled by a variety of processes, including some occurring on the surface of sulfate aerosols [e.g., McElroy *et al.*, 1992].

Increased aerosol loading following the eruption of Mt. Pinatubo in June 1991 led to reduced levels of NO_x, increased concentrations of ClO, and accelerated photochemical removal of O₃ near 20 km consistent with the heterogeneous reaction of N₂O₅ + H₂O being the dominant sink for NO_x [e.g., Fahey *et al.*, 1993; Kawa *et al.*, 1993; Salawitch *et al.*, 1994a,b; Stimpfle *et al.*, 1994]. *in situ* observations of NO, NO_y, O₃, and aerosol surface area [Kondo *et al.*, 1997]; NO₂ and HNO₃ [Webster *et al.*, 1994]; and ClO, NO, and O₃ [Dessler *et al.*, 1993] each show a reduction in NO/NO_y for increased aerosol loading consistent also with chemistry driven largely by the heterogeneous hydrolysis of N₂O₅. However, ground based observations of the decrease in the column abundance of NO₂ and simultaneous increase in column HNO₃ following the eruption of Mt. Pinatubo indicate the need for additional heterogeneous sinks of NO_x to quantitatively account for the measured decrease in NO₂/HNO₃ [Koike *et al.*, 1994]. *In situ* observations of NO, NO₂, ClO, and O₃ at mid-latitudes during the spring of 1993 have revealed a troubling discrepancy in our understanding the NO/NO₂ ratio near 20 km [Jaeglé *et al.*, 1994], although more recent observations over a wider range of latitudes reveal good agreement between theory and observation of this ratio as well

as the NO_x/NO_y ratio [Gao *et al.*, 1997]. Finally, an analysis of *in situ* observations of HCl obtained from 1991 to 1996 suggests heterogeneous reactions other than $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ exert a dominant influence on the composition of the mid-latitude stratosphere [Webster *et al.*, 1997].

The JPL MarkIV Interferometer (MkIV) balloon observations reported here represent the first simultaneous measurements of profiles for all major NO_y species in the same airmass along with the important precursors (e.g., O_3 , CH_4 , H_2O , C_2H_6 , HCl, CO) that allow a stringent comparison to calculated profiles. Furthermore, noon, sunset, and sunrise profiles of NO_x and N_2O_5 were measured in the same airmass, allowing their diurnal behavior to be examined. Previous studies of diurnal behavior have either only obtained measurements over a limited altitude range [Webster *et al.*, 1990; Kondo *et al.*, 1990], have not measured all the relevant species [Roscoe *et al.*, 1990; Chance *et al.*, 1996], or have not measured them all simultaneously in the same air mass [Russell *et al.*, 1988; Rinsland *et al.*, 1996]

Our analyses of the MkIV observations test our understanding of processes that regulate (a) NO_x , the component of the NO_y that reacts directly with O_3 , (b) HNO_3 , the dominant NO_y species at low altitudes, (c) N_2O_5 , the component that links reactive and reservoir NO_y , (d) HNO_4 , a minor reservoir that tests our understanding of HO_x ($= \text{OH} + \text{HO}_2$), and (e) ClNO_3 , the species that couples reactive nitrogen and chlorine. Additionally, our study focuses on testing our understanding of the processes that regulate the concentration of NO_x between 20 and 40 km altitude, for various degrees of aerosol loading prior to and following the eruption of Mt. Pinatubo. Profiles of aerosol surface area associated with each MkIV flight originate from Stratospheric Aerosol and Gas Experiment II (SAGE 11) analyses of zonal, monthly-mean measurements of extinction [Yue *et al.*, 1994].

Balloon Measurements

The MkIV Interferometer [Toon, 1991] is the latest solar absorption FTIR spectrometer designed at JPL for the purpose of remotely measuring atmospheric composition. Its high spectral resolution (0.01 cm^{-1}) and broad coverage ($650\text{-}56\text{X} \text{ cm}^{-1}$) allow a large number of gases to be measured simultaneously, including NO, NO₂, HNO₃, HNO₄, N₂O₅, ClNO₃, O₃, N₂O, H₂O, CH₄, HCl, HOCl, CO, and C₂H₆.

The solar infrared spectra analyzed in this work were acquired during three balloon flights from Fort Sumner, New Mexico ($34.5^\circ\text{N}, 104.2^\circ\text{W}$) on 27 September 1990 and 25 September 1993, and a flight from Daggett, California ($34.8^\circ\text{N}, 114.8^\circ\text{W}$) on 3 April 1993. For the 25 September 1993 flight, volume mixing ratio (vmr) profiles were retrieved from infrared spectra obtained during payload ascent (near noon), as well as sunset and the following sunrise, providing the opportunity to measure the variations of NO and NO₂ during a daily solar cycle. Only sunset spectra were available for retrieval of vmr profiles for the other flights. An unapodized spectral resolution of 0.01 cm^{-1} was employed for tangent altitudes above $\approx 28 \text{ km}$, at which point it was switched to 0.02 cm^{-1} to allow more rapid sampling, keeping the tangent point separation of successive spectra in the 2 to 3 km range. All flights of the MkIV were accompanied by an *in situ* UV photometer. The Submillimeter Limb Sounder (SLS) instrument, which measures ClO, OH, and HO₂ between altitudes of 35 and 50 km by microwave emission spectrometry [Stachnik *et al.*, 1992], flew on the same gondola for the April and September 1993 flights. The Far Infrared Limb Observing Spectrometer (FILOS) instrument, which measures OH between 35 and 45 km by submillimeter spectroscopy [Pickett and Peterson, 1993], accompanied the MkIV on the September 1993 flight.

Data Analysis

The MkIV data analysis consists of two distinct procedures, which are described further in *Scn et al. [1996]*. Briefly, non-linear least squares fitting is first used to calculate the slant column abundance for each target gas in every spectrum. For gases that absorb in more than one spectral interval, a weighted average slant column is calculated. These slant columns, together with the matrix of computed geometrical slant path distances, are then solved to yield concentration profiles. Although the tangent point separation is typically 2 to 3 km at sunset and sunrise, the vmr profiles were retrieved on a 1 km vertical grid. There are two reasons for this choice: (1) to be compatible with the inputs to the spectral calculations and (2) to maintain the high vertical resolution of the limb profiles immediately below the balloon for which tangent point separation is small and of the ascent profile for which the vertical separation between successive spectra was typically only 0.9 km.

The molecular parameters are taken from the ATMOS linelist compilation [*Brown et al., 1996*], based on HITRAN and updated with new spectroscopic measurements, which incorporate the latest laboratory cross sections for N_2O_5 [*Cantrell et al., 1988*], HNO_4 [*May and Friedl, 1993*], and $ClNO_3$ [*Bell et al., 1992*]. The estimated uncertainties in the accuracy of the linelist parameters [*Brown et al., 1996*] used for $A^T O_V$ gas retrievals range from 8 to 10% for NO and NO_2 , 15% for $ClNO_3$, HNO_3 , N_2O_5 , and 20% for HNO_4 . The uncertainties for O_3 and N_2O are $\approx 5\%$.

The errors of vmr profiles reported in this study represent the 1σ measurement precision combined in quadrature with these spectroscopic accuracies. Other systematic error terms such as pointing; and temperature uncertainties are negligible compared with these two: pointing errors have been minimized by fitting temperature insensitive CO_2 lines, and temperature errors minimized by using temperature sensitive CO_2 lines. The measurement precision is calculated during the retrieval process based on considerations such as residuals in spectral fitting. In general, gases with numerous,

strong, well-isolated spectral lines (e. g., O_3 , NO, NO_2 , HNO_3) yield precisions in their retrieved vmr of typically $\approx 5\%$ of the peak vmr. *Abrams et al.* [1996] report similar uncertainties in the accuracy of gases measured by ATMOS, obtained also using high-resolution infrared solar occultation spectra.

For NO and NO_2 , whose concentration varies along the line of sight due to the changing solar zenith angle, diurnal correction matrices were calculated by the photochemical model described below for conditions (e.g., temperature, O_3 , appropriate for the occultations [*Newchurch et al.*, 1996]). Figure 1 compares profiles of NO and NO_2 retrieved with (solid line) and without (dashed line) these diurnal corrections. The large fractional variations of NO at sunset result in significant differences between its two profiles, especially below 25 km. However, for NO_2 , whose fractional variation at sunset is smaller, the diurnal correction makes little difference. In fact, less than 10% error is made by ignoring the diurnal variation of NO_2 for altitudes below 25 km. These results are in accordance with previous work on diurnal correction [*Boughner*, 1980; *Roscoe and Pyle*, 1987; *Russell et al.*, 1988; *Newchurch et al.*, 1996]). The elements of these correction matrices are simply ratios of calculated concentrations at different solar zenith angles and altitudes. Therefore, the absolute values of model concentrations are not communicated to the retrieval algorithm, and therefore cannot bias the retrieved profiles. From the good agreement achieved between our photochemical model and *in-situ* measurements near the terminator [*Salawitch et al.*, 1994b; *Newchurch et al.*, 1996]), we believe that for NO_2 , and for NO above 25 km, the diurnal corrections are not a significant source of uncertainty. The good agreement between diurnally corrected profiles for NO from 18 to 21 km measured by ATMOS and nearly simultaneous *in situ* measurements of NO suggests the diurnal correction procedure yields accurate retrievals at altitudes above 18 km [*Newchurch et al.*, 1996]).

Photochemical Model

The photochemical model has been used previously in many stratospheric studies [e.g., *McElroy et al.*, 1992]. Reaction rates and absorption cross sections are adopted from the JPL 94-26 compendium [*DeMore et al.*, 1994]. The abundance of radical (i.e., NO, NO₂, OH, HO₂, ClO, BrO) and reservoir (i.e., HNO₃, HCl, N₂O₅, ClNO₃) gases has been calculated allowing for diurnal variation and assuming a balance between production and loss rates of each species integrated over a 24 hour period, for the latitude and temperature of the observations. Concentrations of precursors (i.e., O₃, H₂O, CH₄, CO, C₂H₆), the total abundance of NO_y, and Cl_y (\approx HCl + ClO + HOCl + ClNO₃) are constrained to match observations of MkIV and SLS, which measured ClO from the same gondola. The temperature profile was obtained from the MkIV analysis of temperature sensitive CO₂ absorptions, and for September 1993 equaled 216, 222, and 230 K at 22, 26, and 32 km, respectively. The input O₃ profile is based on observations by MkIV, SLS, and an *in situ* UV photometer (Figure 2) and is discussed in detail by *Osterman et al.* [1997].

All heterogeneous reactions on sulfate aerosols believed to affect partitioning of stratospheric NO_y and Cl_y at mid-latitudes were included in the model. Heterogeneous hydrolysis of N₂O₅ was assumed to occur with a reaction probability of 0.1 [*DeMore et al.*, 1994]; the formulation of *Hanson et al.* [1996] was used for the heterogeneous rate of BrNO₃ + H₂O; and the formulations of *Ravishankara and Hanson* [1996] were used for the remaining sulfate heterogeneous reactions (HCl + ClNO₃, HOCl + HCl, and ClNO₃ + H₂O). Kinetic parameters for HOBr + HCl heterogeneous reaction are from *Hanson and Ravishankara* [1995]. Profiles of aerosol surface area originate from zonal, monthly-mean observations of SAGE II [*Yue et al.*, 1994].

Results and Discussion

Accurate measurements of ozone are a prerequisite for quantifying our understanding of nitrogen oxides. Not only does O_3 directly affect the NO/NO_2 and NO_2/HNO_3 ratios, but it also influences many other radicals (e.g., ClO , OH) that interact with NO_x and NO_y . Figure 2 shows a comparison of the sunset profile of ozone measured by MkIV on 25 September 1993, and ascent and descent profiles observed by the *in situ* UV sensor on board the same gondola. The two *in situ* measurements of O_3 , obtained ≈ 20 hours apart and separated by 200 km, agree to better than 5%. This indicates relatively quiescent conditions in the stratosphere during the time of observation, typical for $35^\circ N$ during fall. The excellent agreement between the *in situ* and remote observations of O_3 , better than 6% for all altitudes above 20 km, provides confidence the O_3 profile is not a major source of uncertainty in the model calculations of the apportionment of nitrogen oxides into member species. Since all the gases measured by MkIV are analyzed with the same spectral fitting and retrieval algorithms, the good agreement for O_3 and also for N_2 lends confidence that the other gases, for which no direct validation is possible, are also retrieved accurately. The excellent agreement between ATMOS (using a measurement and data analysis technique similar to MkIV) and *in situ* measurements of N_2O , CH_4 , H_2O , NO_y , O_3 , CFC11, CFC12, CCl_4 , and SF_6 further demonstrate the accuracy achievable by the solar occultation technique [Chang *et al.*, 1996a,b].

NO_y Partitioning and Budget

Observed and theoretical vmr profiles of NO_y species at sunset are illustrated in Figure 3. Profiles for N_2O_5 at sunrise are also shown. Calculated profiles of NO_y species not observed by MkIV (NO_3 , $BrNO_3$, and HNO_2) make only small contributions to the total budget, and are therefore not shown. Overall, the agreement between observed and calculated profiles for all NO_y species is good. The only significant systematic disagreement is for NO_2 below 28 km, where measured values exceed calculated values

by up to 30%. For most of this altitude range, there is good agreement (better than 10%) between observed and calculated vmrs of NO and HNO₃. Consequently, the observed ratios NO₂/NO and NO₂/HNO₃ exceed theoretical estimates below 28 km. The apparent disagreement between observed and modeled NO at 20 km could result from an imperfect diurnal correction, which is not included in our estimate of the error bars and could be very large at this altitude.

The comparisons shown in Figure 3 demonstrate good understanding of most reactive and photolytic processes that regulate the abundance of nitrogen oxides, particularly for altitudes above 28 km. The observed buildup of N₂O₅ during the night as well as its value at the evening terminator are simulated accurately, suggesting the coupling between NO_x and HNO₃ is being treated in a realistic manner by the model. The range of altitudes for which NO, NO₂, and HNO₃ are calculated to be the dominant species of the NO_y family agrees with observations, as does the concentration of each gas for these altitudes. This suggests the height dependence of the concentration of atomic oxygen and the photolysis rate of NO₂ are represented accurately by the model above 28 km, and the production and loss processes for HNO₃ are represented accurately at lower altitudes. The proper treatment of HO_x above 28 km is supported by the agreement between observed and theoretical profiles of NO₂ and HNO₄ (produced by the reaction of NO₂ with HO₂), as well as comparisons with vmrs of OH and HO₂ observed by different instruments from the same gondola [*Pickett and Peterson, 1996; Osterman et al., 1997*].

Two simulations of ClNO₃ are illustrated in Figure 3. The nominal case (solid line) assumes a 7% yield of HCl from ClO + OH and the *Michelsen et al.* [1994] formulation for the quantum yield of O(¹D) from O₃ photolysis, while the other (dashed line) assumes a 0% HCl yield and the *DeMore et al.* [1994] formulation of O(¹D) quantum yield. Only the nominal case is shown for simulations of other species, since calculated profiles are insensitive to the choice of these two kinetic parameters. The vmr profile

of ClNO_3 observed by MkI V generally lies between the two theoretical calculations. A 7% yield of HCl was reported to be consistent with: (1) ATMOS observations of HCl and ClNO_3 [Michelsen *et al.*, 1996], (2) FIRS-2 measurements of HCl and HOCl obtained during 26 September 1989 [Chance *et al.*, 1996], and (3) SLS measurements of ClO during the September 1993 balloon flight [Osterman *et al.*, 1997]. While the MkIV measurements are not inconsistent with a 7% yield of HCl, they suggest a smaller yield for reasons not fully understood [Jaeglé, 1995].

The photochemical model simulation shown in Figure 3 have been constrained to match the total amount of NO_y measured by MkIV at each altitude, as discussed above in the model description section. MkIV also obtains simultaneous measurements of the concentration profile of N_2O , the source of NO_y . Figure 4 illustrates the relation between NO_y and N_2O observed by MkIV, as well as the relation measured by *in situ* instruments aboard the ER-2 aircraft at northern mid-latitudes during February and November, 1994. The *in situ* determination of NO_y is ascribed a 1σ total uncertainty of better than 10% [Fahey *et al.*, 1989], while the *in situ* measurement of N_2O has an estimated 1σ total uncertainty of 3% [Locwenstein *et al.*, 1989]. Theoretically, NO_y and N_2O are expected to exhibit a compact, near linear relation in the lower stratosphere since the rate for redistribution by transport is short compared to photochemical production and loss of each quantity [Plumb and Ko, 1992]. The two measurements of NO_y versus N_2O agree to within the uncertainty of the observations: each is consistent with a slope of -0.07 for $160 < \text{N}_2\text{O} < 310$ ppbv, similar to two dimensional model simulations [Keim *et al.*, 1997]. These comparisons corroborate the accuracy of the MkIV retrievals of the major NO_y species (e.g., HNO_3 , NO_2 , and NO) for the altitudes at which they are dominant. Furthermore, the MkIV relation also illustrates the decrease of NO_y with decreasing N_2O at altitudes above 33 km, due to the rapid (with respect to transport) loss of NO_y by the reaction of $\text{N} + \text{NO}$.

NO_x Chemistry

The reactions [*Crutzen, 1970; Johnston, 1971*]



constitute the primary chemical loss process for stratospheric ozone between altitudes of approximately 24 to 36 km [e.g., *Jucks et al., 1996; Osterman et al., 1997*]. Understanding the processes that regulate NO, NO₂, and NO_x is central to understanding the chemistry of stratospheric O₃. Loss of NO occurs primarily by reaction (1), with a small contribution from



Removal of NO₂ occurs mainly by

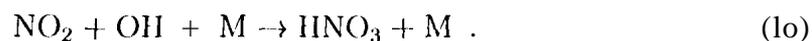
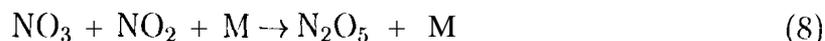
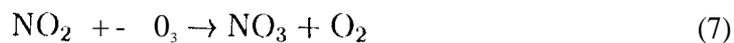


which is much faster than loss by reaction (2) for altitudes below 35 km. Since production and loss of NO and NO₂ occur rapidly, the ratio of the concentration of these species is expected to be described by the instantaneous value of

$$\frac{\text{NO}}{\text{NO}_2} = \frac{J_{\text{NO}_2}}{(k_1 \cdot [\text{O}_3] + k_4 \cdot [\text{m}])} \quad (6)$$

where J_{NO_2} is the photolysis rate of NO₂, and k_1 and k_4 are rate constants for the respective reactions.

Changes in NO_x occur much more slowly than the time for equilibration of NO and NO_2 . Removal of NO_x occurs mainly by production of N_2O_5 and HNO_3 :



Resupply of NO_x occurs by photolysis of N_2O_5 and HNO_3 , and by reaction of HNO_3 with OH . Between altitudes of 26 and 40 km, changes in the concentrations of NO_x and N_2O_5 are expected to exhibit a 2:1 stoichiometry, because N_2O_5 is the dominant nighttime reservoir of NO_x . At lower altitudes, the stoichiometry is expected to exceed 2:1 because, even though reaction (9) is the dominant process by which NO_x is converted to HNO_3 [e.g., *McElroy et al.*, 1992; *Fahey et al.*, 1993], a fraction of NO_x is converted to HNO_3 by reaction (10).

MkIV observations of NO_x and N_2O_5 test, out understanding of the diurnal variation of reactive nitrogen. Measured concentrations of NO_x and $2 \cdot \text{N}_2\text{O}_5$ at sunrise and sunset for three altitudes are shown in Figure 5. Also shown are midday measurements of NO_x , obtained during balloon ascent and retrieved using the same procedures as the sunset and sunrise profiles, taking into account the fundamental difference in observation geometry. The midday profile of N_2O_5 could not be retrieved since the airmass was too small to provide sufficient absorption in ascent spectra.

Theoretical curves for the diurnal variation of NO_x and N_2O_5 are shown also in Figure 5. The solid curves are results of independent simulations constrained by

measured concentrations of precursors at sunset, (red line) and sunrise (blue line), assuming a cloud-free atmosphere with an albedo of 0.24. The shaded region indicates the sensitivity of model results to variations in albedo: highest values of NO_x are calculated assuming high altitude, highly absorbing clouds (albedo=0.2), while lowest values are found assuming highly reflecting clouds (albedo=0.8). Changes in albedo were allowed to impact all photolytic processes (e.g., J_{NO_2} , which affects the NO/NO_2 ratio on rapid time scales, as well as J_{HNO_3} , which affects NO_x/HNO_3 on longer time scales) and is meant to quantify, in a simple manner, the uncertainty of model results associated with the photolytic environment experienced by air parcels during the observation and days immediately prior to it. The atmosphere was cloud free in the MkIV field of view when the sunset spectra were obtained (spectra were recorded for tangent heights as low as 6 km), but contained high-altitude thunderstorm clouds during sunrise.

The results shown in Figure 5 demonstrate a fundamentally good understanding of the coupling between stratospheric NO_x and N_2O_5 . Observed values of NO_x and N_2O_5 agree with theory at 32 km, to within the measurement and model uncertainties. Similarly, observed values of NO_x at sunrise and N_2O_5 at sunset for 26 km agree with model values. However, at this altitude observations of both NO_x at midday and sunset as well as N_2O_5 at sunrise exceed model values, although theory and observation slightly overlap given their respective uncertainties. MkIV observations of variations in concentrations of NO_x and N_2O_5 at both 26 and 32 km exhibit the expected 2:1 stoichiometry. During sunset at 22 km, observation of NO_x exceed theory, and N_2O_5 is less than theory, by amounts roughly consistent with the expected stoichiometry.

As discussed previously the only significant discrepancy in this study is the tendency of observed NO_2 to exceed model values below 28 km (e. g., Figure 3). The strong and well defined infrared absorptions of NO_2 make it one of the more easily measured gases in the MkIV spectra. Two separate bands at 1600 and 2900 cm^{-1} are used to retrieve NO_2 , and the resulting profiles are consistent to better than 10% for all altitudes, and

better than 5% below 27 km. The profile of NO_2 shown in Figure 3 is a weighted average of retrievals from both bands. The good agreement between measured and calculated NO_2 above 30 km, where pressure broadening of the NO_2 absorption features is negligible, indicates that errors in the NO_2 line strengths are unlikely to be the cause of the discrepancy at lower altitudes. A 40% increase in the pressure-broadened half-widths (PBHW) of the NO_2 lines would greatly improve the agreement between calculated and measured NO_2 , since its effect on retrieved vmr would increase with pressure. However, this increase exceeds the 15% uncertainty of the PBHW estimated from laboratory measurements [Brown *et al.*, 1996]. Recent laboratory measurements of the PBHW of NO_2 (D. Newnham, RAL, personal communication, 1997) indicate that the actual values may be 10 to 15% larger than those used in this analysis. Although this would decrease the retrieved MkIV NO_2 concentrations in the lower stratosphere by $\approx 10\%$, a significant disagreement would still remain.

Our estimate of the total uncertainty of the MkIV measurement of NO_2 varies from 19% at 20 km to 11% at 30 km. Therefore, the discrepancy between observations and theory is significant below 28 km. Additionally, NO and HNO_3 are measured with sufficient accuracy and precision in the lower stratosphere that the discrepancy between theory and observation of NO/ NO_2 and NO_2/HNO_3 is also larger than the measurement uncertainty below 28 km.

Figure 6 illustrates co-located measurements of NO, NO_2 and their ratio by HALOE (Version 18, 33.6°N, 110°W) 24 hours earlier and 100 km distant from the MkIV observations on 25 September 1993. The HALOE measurements of NO are based on absorption in the 1900 cm^{-1} band, the same as used by the MkIV. The HALOE measurements of NO_2 are based on absorption in the 1600 cm^{-1} band, one of the two bands used in the MkIV analysis. The estimated total uncertainties of individual retrievals of NO and NO_2 by HALOE are 40% and 26%, respectively, at 22 km [Gordley *et al.*, 1996, Figures 7 and 8]. The measurements of NO, NO_2 and their ratio by the

two remote sensing instruments agree to within 10% above 27 and 25 km, respectively. Theoretical profiles are also shown in Figure 6. Between 23 and 34 km, the MkIV and HALOE measurements of NO_2 are both larger than the model values. Below 23 km, the larger uncertainties associated with the measurements make it difficult to draw any definitive conclusions.

The disagreement between NO_2 measured by MkIV and the calculated values exhibits a similar pattern with respect to altitude for all balloon flights analyzed to date, as shown in Figure 7. These flights sampled air with substantially different levels of aerosol loading, reflecting the relatively clean period prior to the eruption of Mt. Pinatubo, and the subsequent build-up and decline of volcanic aerosol. This suggests the NO_2 discrepancy is not related to transient phenomena such as the possible effect of Mt. Pinatubo aerosol on the photolysis rate of NO_2 . Recent ATMOS measurements obtained in November 1994 at high southern latitudes with relatively low aerosol loading reveal a similar pattern of excess NO_2 with respect to model profiles [Rinsland *et al.*, 1996, Figure 3]. Similarly, nighttime measurements of NO_2 obtained by UV-Vis spectroscopy in March 1994 at 44° N latitude also exhibit an excess over calculated values in the 22 to 28 km altitude range [Renard *et al.*, 1997]. However, an analysis of earlier ATMOS observations obtained at mid-latitudes during April/May 1985 does not reveal a similar discrepancy for NO_2 [e.g., McElroy *et al.*, 1992, Figures 10 and 12].

Figure 8 illustrates the variation with respect to solar zenith angle of MkIV observations of NO , NO_2 and the NO/NO_2 ratio at altitudes of 32, 26, and 22 km. The model simulations are similar to those shown in Figure 5, for sunset (red line) and sunrise (blue line) constraints and a cloud-free albedo of 0.24. The shaded regions represent the sensitivity of calculated values to variations in albedo as discussed previously. The observed concentrations of NO agree with theory, to within the measurement and model uncertainty, at all altitudes and times except for 26 km at sunrise. However, the precision of the midday observations of NO is poor below 26 km owing to the low air

mass factor of the ascent spectra. Similarly, the noontime measurements of NO_2 below 27 km are not sufficiently accurate or consistent to ascertain whether they agree better with the model, or with the 20-30% excess over the model values at sunrise and sunset.

The observed NO/NO_2 ratio is lower than model values at sunrise and sunset for altitudes below 26 km (Figure 8). The calculated photolysis rate of NO_2 agrees well with photolysis rates inferred from observations of the direct and diffuse flux of radiation between 300 to 775 nm from the ER-2 aircraft [McElroy *et al.*, 1995] for solar zenith angles as high as 80° at 20 km [Gao *et al.*, 1997, Figure 4]. Therefore the photolysis rate of NO_2 is unlikely to cause the discrepancy in NO/NO_2 ratio illustrated in Figure 8. Since loss of NO at 22 km by reaction with O_3 proceeds at a rate about four times faster than loss by reaction with ClO , and theory and observation of ClO are in reasonable agreement [Avallone *et al.*, 1993; Salawitch *et al.*, 19(14a); Chang *et al.*, 1996a], it is unlikely that uncertainties in the kinetics of reaction (4) or in the abundance of ClO will resolve the dilemma posed by the observations of NO/NO_2 .

Figure 9 illustrates the recommended value for the rate constant of the reaction $\text{NO} + \text{O}_3$ from the JPL compendium, as well as its nominal 1σ uncertainty [DeMore *et al.*, 1994] as a function of inverse temperature. Also shown are individual laboratory measurements used in the determination of the recommended rate. The recommended uncertainty of the rate is $\approx 50\%$ for a temperature of 220 K [DeMore *et al.*, 1994], considerably larger than the standard deviation about the mean of the individual measurements at this temperature. Also shown is the reaction rate required to balance, in the absence of any other kinetic changes, the NO/NO_2 ratio observed by MkIV at sunset. We do not intend to imply by this figure that rate constants can be determined from atmospheric measurements. It is merely a way of illustrating the uncertainty in the model calculation, and its relationship to laboratory and atmospheric observations. The rate required to balance the observed NO/NO_2 ratio below 23 km is larger than allowed by the laboratory observations, and consequently uncertainties in this rate are an

unlikely explanation for the observed ratio at the lowest altitudes. However, it is difficult to rule out, the possibility, based on the individual laboratory measurements, that the true rate of reaction (1) is 20% faster than the recommended value for temperatures near 216 K, which would explain the measured NO/NO₂ ratios at sunrise and sunset between altitudes of 24 to 32 km.

In situ observation from the ER-2 aircraft of NO (by chemiluminescence) and NO₂ (by chemiluminescence and by a '111,S) at mid-latitudes obtained during SPADÉ (May 1993) indicated a discrepancy between theory and observation of the NO/NO₂ ratio near 20 km during midday of $\approx 35\%$ [Jaeglé *et al.*, 1994], but in the *opposite sense* of the discrepancy noted for the MkIV occultations. However, more recent measurements of NO and N(3₂, obtained at mid-latitudes near 20 km during ASHOE/MAESA (February to November, 1994) using the *in situ* chemiluminescence detector, agree with the theoretical ratio to better than 8% [Gao *et al.*, 1997].

The MkIV observations suggest a discrepancy in our understanding of the NO/NO₂ ratio. For illustrative purposes only, we have calculated the abundance of NO_y gases at 22 km allowing for a 40% reduction in J_{NO₂} at all solar zenith angles, which forces agreement with the measured NO/NO₂ ratio. Results shown in Figure 8 indicate that, even though the NO/NO₂ ratio is simulated correctly, the model values of both NO and NO₂ remain significantly lower than observation. To simultaneously match constraints posed by MkIV observations of NO/NO_y, NO₂/NO_y, and NO/NO₂ at 22 km requires not only a reduction in J_{NO₂} (or, equivalently, an increase in k₁), but also either a reduction in the rate of the heterogeneous hydrolysis of N₂O₅ [reaction (10)] from the recommended reaction probability of 0.1 [DeMore *et al.*, 1994] to a value as low as 0.02, or else accelerated removal of HN03.

Lary *et al.* [1997] have postulated that heterogeneous processes occurring on the surface of carbonaceous soot particles may convert HNO₃ to NO₂. If this process could act rapidly enough to compete with the loss of NO_x by reaction (10), it would offer an

explanation for the tendency of the MkIV observations of NO_2 to exceed model values. However, this reaction would cause serious difficulties in accounting for a wealth of observations of the NO/NO_y ratio obtained from the ER-2 [Salawitch *et al.*, 1994a,b; Gao *et al.*, 1997] as well as our observation of the NO/HNO_3 ratio above 22 km. Simultaneous measurements of NO and NO_2 by instruments on the ER-2 and MkIV for the same air masses during the upcoming POLARIS campaign will hopefully shed additional light on our understanding of the processes that regulate NO_x .

The effect of Mt. Pinatubo aerosols on NO_x

Increases by factors of 20 to 30 in the surface area of sulfate aerosol following the June 1991 eruption of Mt. Pinatubo [e.g., McCormick *et al.*, 1995] reduced levels of NO_x throughout the stratosphere due to reaction (10), the heterogeneous hydrolysis of N_2O_5 [e.g., Fahey *et al.*, 1993; Webster *et al.*, 1994]. The reduction in $\text{A}^\text{T}\text{OX}$ led to increases in concentrations of ClO and HO_x , increasing the overall efficiency of catalytic removal of O_3 by reactive nitrogen, chlorine, and hydrogen species in the lower stratosphere [e.g., Kinnison *et al.*, 1994; Rodriguez *et al.*, 1994]. Previous analyses of observations of NO and NO_y from the ER-2 [Fahey *et al.*, 1993; Kawa *et al.*, 1993; Salawitch *et al.*, 1994a,b; Gao *et al.*, 1997] suggested that reaction (10) is the dominant sink for NO_x throughout much of the lower stratosphere following the eruption of Mt. Pinatubo. Similar conclusions were reached based on analysis of balloon-borne observations of NO_2 and HNO_3 [Webster *et al.*, 1994] as well as NO and NO_y [Kondo *et al.*, 1997]. However, Koike *et al.* [1994] observed larger increases in the column abundance of HNO_3 , and decreases in column NO_2 , than could be accounted for by reaction (10) alone. The variation of *in situ* observations of HCl with aerosol surface area has been interpreted as evidence for a dominant influence by heterogeneous reactions involving HCl and ClNO_3 [Webster *et al.*, 1997]. Furthermore, Solomon *et al.* [1996] showed that the observed decline in O_3 during the past several decades, due to both the build up of chlorine from

industrial CFCs and changes in sulfate aerosol loading, was about 50% larger than calculated by their two-dimensional model. Similarly, *Kinnison et al.* [1994] are unable to account for the magnitude of the observed reduction of O_3 following the eruption of Mt. Pinatubo when both the radiative and chemical effects of volcanic aerosol are considered.

We present observations of NO , NO_2 , and NO_y by MkIV for three balloon flights encountering vastly different levels of sulfate aerosol loading. These observations provide a test of our understanding of the heterogeneous chemistry associated with Mt. Pinatubo aerosols on the NO_x/NO_y ratio. We seek to establish whether the observations provide evidence that other heterogeneous sinks of NO_x besides reaction (10) exert a substantial influence on the chemistry of the mid-latitude stratosphere. If so, loss of O_3 due to Mt. Pinatubo aerosols would likely exceed model predictions [e.g., *Prather*, 1992].

Figure 10 compares the measured profiles of NO_x/NO_y at sunset to theoretical profiles for flights of MkIV during September 1990, April 1993, and September 1993. Also shown are the profiles of sulfate aerosol surface area associated with each MkIV flight, derived from SAGE II zonal, monthly-mean measurements of extinction in the visible and near ultraviolet [Yue et al., 1994]. The theoretical curves are constrained by profiles of O_3 , H_2O , CH_4 , NO_y , $HCl + ClNO_2 + HOCl$, temperature, etc. measured by MkIV for each flight and the SAGE II surface area profile shown in Figure 10. Three model curves for NO_x/NO_y are shown for each flight: results of (1) a purely gas phase calculation (solid line), (2) gas phase + N_2O_5 hydrolysis (reaction 10) only (dotted line), and (3) gas phase + all heterogeneous reactions (dashed line). Calculated values of the NO_x/NO_y ratio are nearly identical for the two heterogeneous simulations because temperatures encountered during the three flights were too warm (209.1, 211.0, and 209.1 K at 20 km for September 1990, April 1993, and September 1993) and aerosol surface areas too low for loss of NO_x by the two heterogeneous reactions involving

ClNO_3 [e.g., *Ravishankara and Hanson, 1996*]. The small difference between the two heterogeneous simulations is predominantly due to the reaction of $\text{BrNO}_3 + \text{H}_2\text{O}$. This reaction does not become an efficient sink of A^+OX for levels of aerosol loading encountered during April 1993 and contemporary levels of Br_y [e.g., 17.9 pptv at 22 km for April 1993] until air parcels reach latitudes poleward of 50° , where the less intense photolytic environment results in slower rates for competing processes [*Tie and Brasseur, 1996*].

The height dependence of the observed NO_x/NO_y ratio agrees fairly well with profiles calculated using the heterogeneous models, although the observed ratio exceeds theory between altitudes of 23 and 30 km. For this range of altitudes, the observations agree more closely, in general, with the ‘gas phase only’ calculations. For altitudes below 23 km, measured values of this ratio agree well with the ‘heterogeneous’ simulations and are appreciably smaller than the ‘gas phase only’ calculations, consistent with conclusions of numerous previous studies [e. g., *McElroy et al., 1992; Dessler et al., 1993; Fahey et al., 1993; Webster et al., 1994; Ito et al., 1997*].

It is tempting to contemplate the existence of a neglected process that converts HNO_3 to NO_x , such as heterogeneous reactions on soot as suggested by Lary et al. [1997], based on the comparisons shown in Figure 10. Likewise, a large reduction in the rate of reaction (10) would also yield better agreement between theory and observation of NO_x/NO_y between 23 and 30 km. However, the observation of excess NO_x relative to the ‘heterogeneous’ model profiles is caused primarily by the discrepancy in NO_2 , as discussed previously. The observed NO/HNO_3 ratio in this altitude range agrees well with profiles calculated using published rates for the heterogeneous reactions listed above [e.g., Figure 3]. Furthermore, the ‘heterogeneous’ model profiles of NO_x/NO_y agree with observed values below 23 km, even though the observed NO/NO_2 ratio is simulated poorly [e. g., Figure 8]. Understanding the cause of the discrepancy between theory and observation of the NO/NO_2 ratio, which should be in near instantaneous

equilibrium with the value of expression (5), is a prerequisite for gaining further insight into the apparent disagreement for NO_x/NO_y between 23 and 30 km.

Figure 11 quantifies the dependence of the NO_x/NO_y ratio on aerosol surface area for each flight. The model curves are identical to those shown in Figure 10. Aerosol surface area is used as the abscissa for all model results, even though it has little bearing on the gas phase simulation. The gas phase calculation captures the non-linear dependence of the observed NO_x/NO_y ratio for surface area less than $\approx 0.6 \mu\text{m}^2\text{cm}^{-3}$, primarily due to the influence of O_3 , and consistently overpredicts the magnitude of the ratio at larger values of surface area. The abundance of O_3 controls both the apportionment of NO_x between NO and NO_2 and the nighttime formation of N_2O_5 . Since the nighttime formation of N_2O_5 occurs by the reaction of NO_2 and NO_3 (i.e., quadratically dependent on NO_x), the NO_x/NO_y ratio is expected to eventually become insensitive to increases in surface area beyond a critical value, provided $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ is the dominant sink for NO_x . The calculations in Figure 11 suggest this critical value is $\approx 4 \mu\text{m}^2\text{cm}^{-3}$ for the conditions encountered during the balloon flights. This critical value together with the NO_x/NO_y ratio at saturation are consistent with previous balloon and airborne chemiluminescence observations of NO and NO_y [Dessler *et al.*, 1993; Fahey *et al.*, 1993; Kondo *et al.*, 1997] and suggest $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ is the dominant sink of NO_x for the sampled air masses.

Conclusions

Observations obtained at mid-latitude (35°N) during the September 1993 balloon flight of the JPL MkIV interferometer, and aerosol surface area basin] on SAGE II extinction measurements, have been examined to assess our understanding of the NO_y budget and partitioning of NO_y species. The variation of the total nitrogen content for the individual NO_y species relative to N_2O agrees well with *in situ* observations and previously published relations found using two dimensional models. The MkIV

observations provide an important test for models since they extend to considerably higher altitudes than the *in situ* observations.

MkIV observations of NO, NO₂, and HNO₃ agree well with theoretical profiles for the range of altitudes that each gas is the dominant NO_y species. Our observations of the diurnal variation of NO_x and N₂O₅ exhibit close agreement with the theoretical stoichiometry between 20 and 40 km, suggesting the coupling between NO_x and its dominant, nighttime reservoirs is well understood. Measured vmr profiles of all NO_y species agree well with model profiles, except that, the observed abundance of NO₂ in the lower stratosphere exceeds calculated values by 20 to 30%. The resulting discrepancies between theory and observation of the NO/NO₂ and NO₂/HNO₃ ratios for altitudes between 20 and 28 km are larger than the estimated total uncertainty (accuracy and precision) of the measurements. Published uncertainties in laboratory measurements of the absorption cross section of NO₂ [DeMore *et al.*, 1994] and the rate of NO + O₃ are individually smaller than the discrepancy for the NO/NO₂ ratio below 23 km. However, a 10% increase in the rate of NO + O₃ at cold temperatures, together with a 10% increase in the pressure-broadened half-widths of the NO₂ lines, both of which appear plausible, would lead to substantial improvement in agreement between observed and calculated NO₂ in the lower stratosphere, but still leave a difference of ≈10%.

The comparison between observation and theory for three MkIV balloon flights before (September 1990) and after (April and September 1993) the eruption of Mt. Pinatubo suggests that N₂O₅ hydrolysis alone can describe the observed NO_x/NO_y ratio. Additional heterogeneous reactions do not perturb this ratio appreciably for surface area below 14 × 10²¹ cm² for the temperatures (209 to 219 K) of our mid-latitude observations. Our analysis of these observations suggests heterogeneous reactions involving ClNO₂ and HCl are not a significant sink for mid-latitude NO_x, which had been a possible explanation for the quantitative anomalies of column NO₂ and HNO₃ presented by Koike *et al.* [1994]. The observed saturation of NO_x/NO_y ratio limits

the increase of ClO within the Cl_y reservoir. *Osterman et al.* [in preparation] show that MkIV observations of HCl and ClNO₃ at 20 km obtained during the same flights are relatively insensitive to surface area, providing further evidence that heterogeneous reactions involving ClNO₃ and HCl do not proceed rapidly enough to significantly alter NO_x or ClO for the sampled air masses. Our observations suggest the decline in reactive nitrogen by volcanic aerosol is well understood and that catastrophic loss of O₃ due to massive enhancements in ClO [e.g., *Prather, 1992*] and large reductions in HCl [*Webster et al., 1997*] is unlikely for the environmental conditions encountered by these balloon flights.

Acknowledgments. The authors wish to thank D.C. Petterson, J.H. Riccio, R.D. Howe, and W. Il. Wilson of JPL for their considerable field support during the balloon campaign. We wish to thank the NSBF which conducted the balloon launches, flight operations and recovery of the payload. We also wish to thank D. W. Fahey (NOAA) for the use of the ER-2 NO_y data, M. Loewenstein (NASA/AMES) for the use of the ER-2 N₂O data, and J.M. Russell, 111 (Hampton University) for the use of the HALOE NO and NO₂ measurements. This research was performed at Jet Propulsion laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

References

- Abrams, M.C. *et al.*, on the assessment and uncertainty of atmospheric trace gas measurements with high resolution infrared solar occultation spectra from space by the ATMOS experiment, *Geophys. Res. Lett.*, **23**, 2337-2340, 1996.
- Avallone, L. M., D.W. Toohey, W.H. Brune, R.J. Salawitch, A.E. Dessler, and J.G. Anderson, Balloon-borne *in situ* measurements of ClO and ozone: implications for heterogeneous chemistry and mid-latitude ozone loss, *Geophys. Res. Lett.*, **20**, 1795-1708, 1993.
- Bell, W., G. Duxbury, and D.D. Stuart, High resolution spectra of ν_4 band of chlorine nitrate, *J. Mol. Spectrosc.*, **152**, 283-297, 1992.
- Boughner, R. J., J.C. Larson, and M. Natarajan, The influence of NO and ClO variations at twilight on the interpretation of solar occultation measurements, *Geophys. Res. Lett.*, **7**, 231-234, 1980.
- Brown, L. R., M.R. Gunson, R.A. Toth, F.W. Irion, C. F. Rinsland and A. Goldman, The 1995 atmospheric trace molecule spectroscopy experiment (ATMOS) linelist, *Appl. Optics*, **35**, 2828-2848, 1996.
- Cantrell, C. A., J.A. Davidson, A.H. McDaniel, R. E. Shetter, and J.G. Calvert, Infrared absorption cross-sections for N_2O_5 , *Chem. Phys. Lett.*, **148**, 358-362, 1988.
- Chance, K. *et al.*, Simultaneous measurements of stratospheric HO_x , NO_x , and Cl_x - comparison with a photochemical model, *J. Geophys. Res.*, **101**, 9031-9043, 1996.
- Chang, A. Y. *et al.*, A comparison of measurements from ATMOS and instruments aboard the ER-2 aircraft: halogenated gases, *Geophys. Res. Lett.*, **23**, 2393-2396, 1996a.
- Chang, A. Y. *et al.*, A comparison of measurements from ATMOS and instruments aboard the ER-2 aircraft: tracers of atmospheric transport, *Geophys. Res. Lett.*, **25**, 2393-2396, 1996b.
- Crutzen, P. J., The influence of nitrogen oxides on the atmospheric ozone content, *J. Roy. Met. Soc.*, **96**, 320-325, 1970.
- DeMore, W. I. *et al.*, Chemical kinetics and photochemical data for use in stratospheric modeling, *JPL Publ.* **94-26**, 1994.

- Dessler, A.E. *et al.*, Balloon-borne measurements of ClO, NO, and O₃ in a volcanic cloud - an analysis of heterogeneous chemistry between 20 and 30 km, *Geophys. Res. Lett.*, *20*, 2527-2530, 1993.
- Fahey, D.W. *et al.*, *In situ* measurements constraining the role of sulfate aerosols in mid-latitude ozone depletion, *Nature*, *363*, 509-514, 1993.
- Fahey, D.W. *et al.*, *In situ* measurements of total reactive nitrogen, total water, and aerosol in a polar stratospheric cloud in the Antarctic, *J. Geophys. Res.*, *94*, 11299-11315, 1989.
- Gao, R.S. *et al.*, Partitioning of the reactive nitrogen reservoir in the lower stratosphere of the southern hemisphere: observations and modeling, *J. Geophys. Res.*, *submitted*, 1997.
- Gordley, L.L. *et al.*, validation of nitric oxide and nitrogen dioxide measurements made by Halogen occultation Experiment for UARS platform, *J. Geophys. Res.*, *101*, 10241-10266, 1996.
- Hanson, D.R., and A.R. Ravishankara, Heterogeneous chemistry of bromine species in sulfuric-acid under stratospheric conditions, *Geophys. Res. Lett.*, *22*, 385-388, 1995.
- Hanson, D.R., A.R. Ravishankara and E. It. Lovejoy, Reactions of BrONO₂ with H₂O on submicron sulfuric acid aerosol and the implications for the lowest stratosphere, *J. Geophys. Res.*, *101*, 9063-9069, 1996.
- Jaeglé, L., Stratospheric chlorine and nitrogen chemistry: observations and modeling, Ph.D. Dissertation, 159 pp., California Institute of Technology, December 1995.
- Jaeglé, L. *et al.*, *In situ* measurements of NO₂/NO ratio for testing atmospheric photochemical models, *Geophys. Res. Lett.*, *21*, 2555-2558, 1994.
- Johnston, H. S., Reduction in stratospheric ozone by nitrogen oxide catalysts from SST exhaust, *Science*, *173*, 517-522, 1971.
- Jucks, K. W. *et al.*, Ozone production and loss rate measurements in the middle stratosphere, *J. Geophys. Res.*, *101*, 28785-28792, 1996.
- Kawa, S. R., *et al.*, Interpretation of NO_x/NO_y observations from AASE-II using a model of chemistry along trajectories, *Geophys. Res. Lett.*, *20*, 2507-2510, 1993.
- Keim, E.R. *et al.*, Measurements of the NO_y - N₂O correlations in the lower stratosphere: latitudinal and seasonal changes and model comparisons, *J. Geophys. Res.*, *submitted*,

- 1997.
- Kinnison, J. I., K.E. Grant, P.S. Connell, D.A. Rotman, and D.J. Wuebbles, The chemical and radiative effects of the Mount Pinatubo eruption, *J. Geophys. Res.*, *99*, 25705-25731, 1994.
- Koike, M. *et al.*, Impact of Pinatubo aerosols on the partitioning between NO₂ and HNO₃, *Geophys. Res. Lett.*, *21*, 597-600, 1994.
- Kondo, Y., T. Sugita, R.J. Salawitch, M. Koike, and T. Deshler, The effect of Pinatubo aerosols on stratospheric NO, *J. Geophys. Res.*, *102*, 1205-1213, 1997.
- Kondo, Y. *et al.*, Diurnal variation of nitric-oxide in the upper-stratosphere, *J. Geophys. Res.*, *95*, 22513-22522, 1990.
- Lary D.J. *et al.*, carbon aerosols and atmospheric photochemistry, *J. Geophys. Res.*, *in press*, 1997.
- Loewenstein, M., J.R. Podolske, K.R. Chan, and S.E. Strahan, Nitrous oxide as a dynamical tracer in the 1987 Airborne Antarctic Ozone Experiment, *J. Geophys. Res.*, *94*, 11589-11598, 1989.
- May, R.D., and R.R. Friedl, Integrated band intensities of HO₂NO₂ at 220K, *J. Quant. Spectrosc. Radiat. Transfer*, *52*, 257-266, 1993.
- McCormick, M. P., L.W. Thomason, and C.R. Trepte, Atmospheric effects of the Mt. Pinatubo eruption, *Nature*, *373*, 399-404, 1995.
- McElroy, C.T., C. Midwinter, D.V. Barton, and R.B. Hall, A comparison of J-values from the composition and photodissociative flux measurement with model-calculations, *Geophys. Res. Lett.*, *22*, 1365-1368, 1995.
- McElroy, M. B., R.J. Salawitch and K. Minschwaner, The changing stratosphere, *Planet. Space Sci.*, *40*, 373-401, 1992.
- Michelsen, H.A. *et al.*, Stratospheric chlorine partitioning: constraints from shuttle-borne measurements of [HCl], [ClNO₃], and [ClO], *Geophys. Res. Lett.*, *23*, 2361-2364, 1996.
- Michelsen, H. A., R.J. Salawitch, P.O. Wennberg, and J.G. Anderson, Production of O(¹D) from photolysis of O₃, *Geophys. Res. Lett.*, *21*, 2227-2230, 1994.
- Newchurch, M.J. *et al.*, Stratospheric NO and NO₂ abundances from ATMOS solar-occultation

- measurements, *Geophys. Res. Lett.*, *23*, 2373-2376, 1996.
- Osterman, G. Il. *et al.*, Balloon-borne measurements of stratospheric radicals and their precursors: implications for production and loss of ozone, *Geophys. Res. Lett.*, *in press*, 1997.
- Pickett, H. M., and D.B. Peterson, Comparison of measured stratospheric OH with prediction, *J. Geophys. Res.*, *101*, 16789-16796, 1996.
- Pickett, H. M., and D.B. Peterson, Stratospheric OH measurements with a far-infrared limb observing spectrometer, *J. Geophys. Res.*, *98*, 20507-20515, 1993.
- Plumb, R.A. and M.K.W. Ko, Interrelationships between mixing ratios of long-lived stratospheric Constituents, *J. Geophys. Res.*, *97*, 1014 -10156," 1992.
- Prather, M., Catastrophic loss of stratospheric ozone in dense volcanic clouds, *J. Geophys. Res.*, *97*, 10187-10191, 1992.
- Ravishankara, A.R. and D.R. Hanson, Differences in the reactivity of type-1 polar stratospheric clouds depending on their phase, *J. Geophys. Res.*, *101*, 3885-3890, 1996.
- Renard, J.-D. *et al.*, Vertical distribution of nighttime stratospheric NO₂ from balloon measurements: comparison with models, *Geophys. Res. Lett.*, *24*, 73-76, 1997.
- Rinsland, C. P., *et al.*, ATMOS/ATLAS-2 measurements of stratospheric chlorine and reactive nitrogen partitioning inside and outside the November 1994 Antarctic vortex, *Geophys. Res. Lett.*, *23*, 2365-2368, 1996.
- Rodriguez, J. M., M.K.W. Ko, N. D. Sze, C.W. Heisey, G.K. Yue, M. P. McCormick, Ozone response to enhanced heterogeneous processing after the eruption of Mt-Pinatubo, *Geophys. Res. Lett.*, *21*, 209-212, 1994.
- Roscoe, H. K., and J. A. Pyle, Measurements of solar occultation: the error in a naive retrieval if the constituent's concentration changes, *J. Atmos. Chem.*, *5*, 323-341, 1987.
- Roscoe, H. K., J.R. Drummond, and R.F. Jarrot, Infrared measurements of stratospheric composition, III, the daytime changes of NO and NO₂, *Proc. R. Soc., London A*, *375*, 507-528, 1981.
- Russell, J.M. *et al.*, Measurements of odd nitrogen compounds in the stratosphere by the ATMOS experiment on Spacelab 3, *J. Geophys. Res.*, *93*, 1718-1736, 1988.

- Salawitch, R.J. *et al.*, The distribution of hydrogen, nitrogen, and chlorine radicals in the lower stratosphere: implications for changes in O₃ due to emission of NO_y from supersonic aircraft, *Geophys. Res. Lett.*, *21*, 2547-2550, 1994a.
- Salawitch, R.J. *et al.*, The diurnal variation of hydrogen, nitrogen, and chlorine radicals: implications for the heterogeneous production of HNO₂, *Geophys. Res. Lett.*, *21*, 2551-2554, 1994b.
- Sen, B., G.C. Toon, J.-F. Blavier, E.L. Fleming, and C. H. Jackman, Balloon-borne observations of mid-latitude fluorine abundance, *J. Geophys. Res.*, *101*, 9045-9054, 1996.
- Solomon, S., R.W. Portmann, R.R. Garcia, L.W. Thomason, and M.P. McCormick, The role of aerosol variations in anthropogenic ozone depletion at northern midlatitudes, *J. Geophys. Res.*, *101*, 6713-6727, 1996.
- Stachnik, R. A., J.C. Hardy, J.A. Tarsala, and J.W. Waters, Submillimeterwave heterodyne measurements of stratospheric ClO, HCl, O₃, and HO₂: first results, *Geophys. Res. Lett.*, *19*, 1931-1934, 1992.
- Stimpfle, R.M. *et al.*, The response of ClO radical concentrations to variations in NO₂ radical concentrations in the lower stratosphere, *Geophys. Res. Lett.*, *21*, 2543-2546, 1994.
- Tie, X. X., G. Brasseur, The importance of heterogeneous bromine chemistry in the lower stratosphere, *Geophys. Res. Lett.*, *23*, 2505-2508, 1996.
- Toon, G. C., The JPL MkIV interferometer, *Opt. Photonics News*, *2*, 19-21, 1991.
- Webster, C. H. *et al.*, Evolution of HCl concentrations in the lower stratosphere from 1991 to 1996 following the eruption of Mt. Pinatubo, *Geophys. Res. Lett.*, *submitted*, 1997.
- Webster, C. R., R. L. May, M. Allen, I. Jaeglé, M.P. McCormick, Balloon profiles of stratospheric NO₂ and HNO₃ for testing the heterogeneous hydrolysis of N₂O₅ on sulfate aerosols, *Geophys. Res. Lett.*, *21*, 53-56, 1994.
- Webster, C.H., R.D. May, R. Toumi, and J.A. Pyle, Active nitrogen partitioning and the nighttime formation of N₂O₅ in the stratosphere - simultaneous *in situ* measurements of NO, NO₂, HNO₃, O₃, and N₂O using the BLISS diode-laser spectrometer, *J. Geophys. Res.*, *95*, 13851-13866, 1990.
- Wernberg, P.O. *et al.*, Removal of stratospheric O₃ by radicals *in situ* measurements of OH,

HO₂, NO, NO₂, ClO, and BrO, *Science*, *266*, 398-404, 1994.

Yue, G.K., L.R. Poole, P.-H. Wang, and E.W. Chiou, Stratospheric aerosol acidity, density, and refractive index deduced from SAGA II and NMC temperature data, *J. Geophys. Res.*, *99*, 3727-3738, 1994.

Figure 1. NO and NO₂ profiles at sunset of 25 September 1993 with and without diurnal corrections. Error bars have been displaced in altitude for visual clarity.

Figure 2. Ozone vmr profiles measured by *in situ* UV sensor during balloon ascent on 25 September 1993 and descent the following day. MkIV measurement of O₃ during sunset of 25 September from the same balloon gondola as the UV instrument is included for comparison between the two measurement techniques.

Figure 3. Observed (symbols) and calculated (lines) vmr profiles of NO_y and member species, as indicated, measured at sunset by MkIV at 35° N on 25 September 1993. Sunrise profiles for N₂O₅ are also shown. The NO_y profile represents only the sum of measured nitrogen oxides.

Figure 4. Correlation of vmrs of NO_y and N₂O measured at sunset by MkIV (25 September 1993) and by instruments aboard the ER-2 aircraft, (14 February and 2, 4 November 1994.)

Figure 5. The midday, sunset and sunrise values for NO_x and 2·N₂O₅ are presented for the altitudes of 32, 26, and 22 km. The calculated values plotted illustrate the behavior of the model (sunset: red lines; sunrise: blue line) during the periods of MkIV measurement and the changes in NO_x due to variations in albedo.

Figure 6. HALOE (triangles) and MkIV measurements at sunset of NO and NO₂ on 25 September 1993. The measurements have been displaced in altitude for visual clarity. The modeled profiles (solid line) of NO and NO₂ from a simulation constrained by MkIV measurements of precursors is included for comparison.

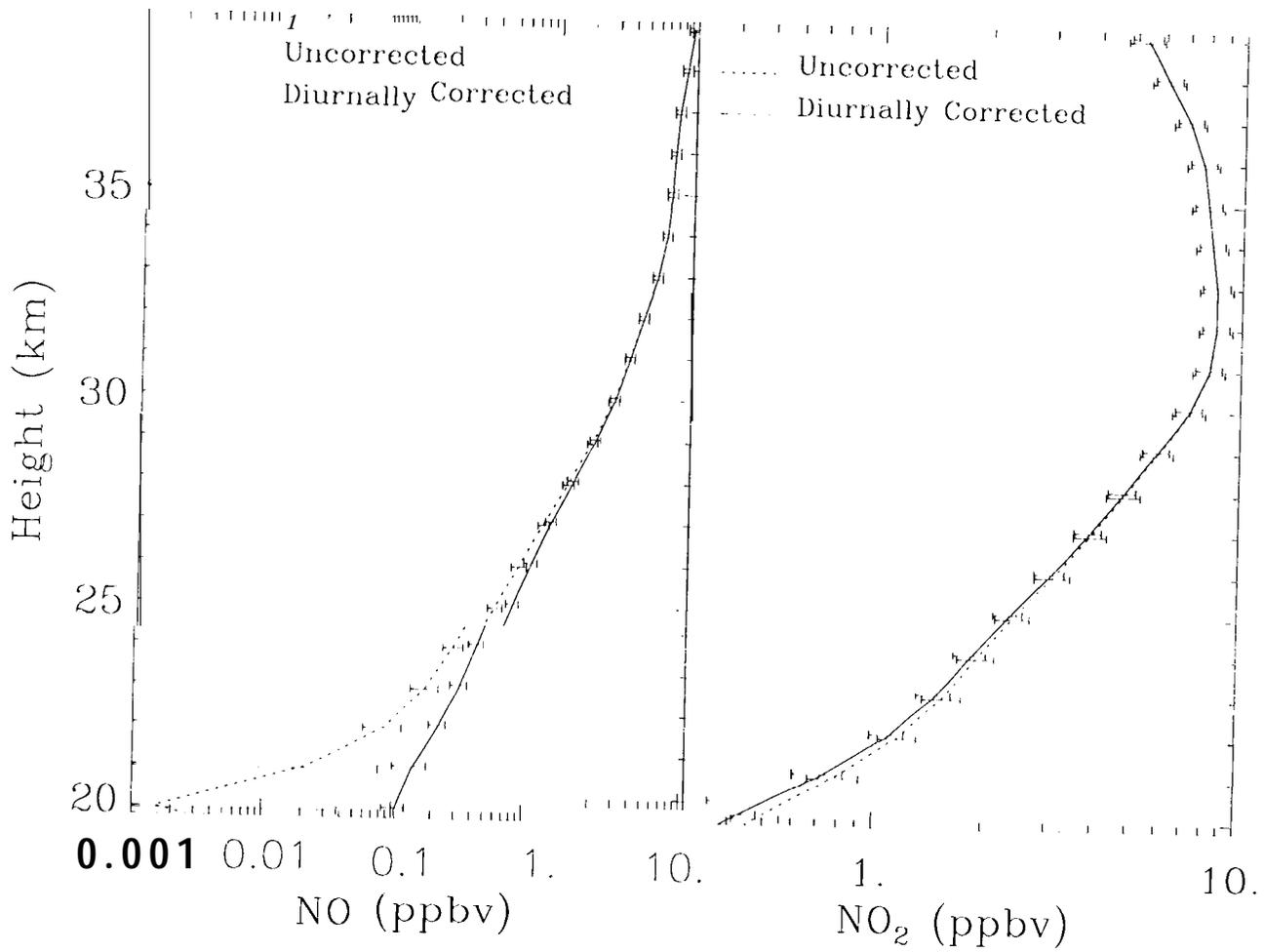
Figure 7. The fractional difference in measured and modeled NO₂ for September 1990, April 1993, September 1993, and May 1994 balloon flights of the MkIV. Model simulations are constrained by the MkIV measurements of precursors appropriate for each balloon flight.

Figure 8. Observed values of NO, NO₂, and NO/NO₂ during sunrise, midday, and sunset during the September 1993 balloon flight. The model curves represent the same simulations illustrated in Figure 5.

Figure 9. Measured and recommended rates of the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$. Recommended rate and its error is from JPL 94-26. Measurements are shown with their respective errors. References to individual measurements are listed in JPL 94-26.

Figure 10. The observed and calculated profiles of NO_x/NO_y as a function of altitude. Results from three balloon flights are shown for differing levels of aerosol surface area: pre Mt. Pinatubo eruption (Ft. Sumner, Sept. 1990) moderate recovery from the eruption (Ft. Sumner, Sept. 1993), highly perturbed loading (Daggett, Apr. 1993). Three simulations describe each balloon flight: (1) gas phase only (solid line), (2) gas phase and N_2O_5 hydrolysis (dotted line), and (3) gas phase and all heterogeneous reactions (dashed line).

Figure 11. The observed and calculated profiles of NO_x/NO_y as a function of aerosol surface area. Note changes in both abscissa and ordinate scale in three panels. The model curves represent the same three simulations illustrated in Figure 10.



Ft. Sumner Balloon Flight 930925 UV in situ and MarkIV Ozone

