ODD NITROGEN DURING THE MAP/GLOBUS 1983 CAMPAIGN: THEORETICAL CONSIDERATIONS*

GUY BRASSEUR†
National Center for Atmospheric Research,‡ Boulder, CO 80307, U.S.A.

DANIEL CARIOLLE
Etablissement d'Etudes et de Recherches Meteorologiques, F-31057 Toulouse, France

ANNE DE RUDDER
Institut d'Aeronomie Spatiale, B-1180 Brussels, Belgium

LESLEY J. GRAY
Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, U.K.

JOHN A. PYLE
University of Cambridge, Department of Physical Chemistry, Cambridge CB2 1EP, U.K.

ERNST-PETER RÖTH
University of Essen, Institute of Physical Chemistry, D-4300 Essen 1, F.R.G.

UTA SCHMAILZL
Max-Planck-Institute for Chemistry, D-6500 Mainz, F.R.G.

and

DONALD J. WUEBBLES
Lawrence Livermore National Laboratory, Livermore, CA 94550, U.S.A.

Abstract—The paper reviews the chemical processes involved in the formation and destruction of active nitrogen in the stratosphere and indicates that transport processes play an important role in the behavior of these species. Vertical profiles measured during the MAP/GLOBUS 1983 campaign are compared to distributions calculated by a number of one-dimensional models. An intercomparison between six of these models shows that, if some quantitative differences attributed to different model input are noticeable, the same type of behavior is predicted for NO and NO_2 by all models. Although the observed concentration of species belonging to the odd nitrogen family should be highly variable, as a result of dynamical disturbances, most data obtained during the campaign appear to be consistent with the chemical scheme currently used in photochemical models.

1. INTRODUCTION

Since the pioneering work of Crutzen (1970) showing the importance of nitrogen oxides for the ozone balance in the stratosphere, considerable work has been devoted to the study of odd nitrogen in the atmosphere. Observations of species such as NO, NO_2 or

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†On leave from the Institut d'Aeronomie Spatiale, B-1180 Brussels, Belgium.
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HNO_3 have shown that the distribution of active nitrogen compounds is governed simultaneously by chemistry, radiation and dynamics. Numerical models have allowed the behavior of these species to be quantified as a function of altitude, latitude and season. Although much progress has been made in the last years, based on *in situ* and satellite observations together with theoretical interpretations through photochemical models, a number of problems remain to be elucidated. For example, the budget of HNO_3 at high latitude in winter or at high altitude is not yet well understood. Also, the amount of odd nitrogen (defined as the total concentration of

$N + NO + NO_2 + NO_3 + 2 \times N_2O_5 + HNO_3 + HO_2NO_2 + ClONO_2$) deduced from the *Nimbus* 7 LIMS experiment (Callis *et al.*, 1986) is about 30% higher than the value provided by most numerical models (about 18 ppbv). Finally, the understanding of the role of N_2O_5 in the budget of odd nitrogen is based essentially on theoretical analyses (Solomon *et al.*, 1984), or on indirect evidences through observations of NO or NO_2 (Knight *et al.*, 1982; Solomon and Russell, 1986), as the vertical distribution of this species has been observed for the first time only very recently (Toon *et al.*, 1986).

One of the purposes of the MAP/GLOBUS 1983 campaign was to measure simultaneously ozone and several nitrogen species (Offermann, 1987). The present paper is intended to present a theoretical background for the interpretation of these observations. As many of these data have been obtained at different times of the day, special attention will be given to the diurnal variation of NO and NO_2. Observations of the diurnal variation in the NO concentration have been reported for many years, by for example Buckhardt *et al.* (1975), Ridley *et al.* (1977) or Ridley and Schiff (1981). Differences in the amount of NO_2 at sunrise and sunset have been noted by Evans *et al.* (1978), by Coffey *et al.* (1981) and others (see WMO/NASA, 1987 for a review). Solomon and Russell (1986) have recently used the *Nimbus* 7 LIMS data from high latitude in summer to study the behavior of NO_2 as a function of solar zenith angle, especially near sunset.

In order to test the consistency of the chemical theory with regard to observed data, vertical distributions of species such as NO, NO_2, NO_3 and HNO_3 measured during the MAP/GLOBUS 1983 campaign will be compared with vertical profiles obtained from model calculations. The discussion will be based on results taken from several representative time-dependent models developed by the authors of this paper. These models are one-dimensional and based on a chemical and photochemical scheme involving the most important reactions related to the chemistry of nitrogen oxides in the atmosphere. The vertical transport is parameterized by means of an eddy diffusion representation. The model inputs such as the boundary conditions, the reaction rate constants, the absorption cross-sections and the transport parameters are similar in all models but not necessarily identical. Therefore the observed vertical distributions will generally be compared to theoretical distributions provided by more than one model. Moreover, a comparison of the diurnal variation of NO_2 calculated by all models involved in the present study will be presented.

2. CHEMISTRY AND PHOTOCHEMISTRY OF NITROGEN OXIDES

Active odd nitrogen is produced in the low- and mid-latitude stratosphere essentially by the oxidation of nitrous oxide:

$$N_2O + O(^1D) \rightarrow 2NO.$$
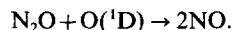
N_2O itself is produced principally by bacterial processes associated with complex nitrification and denitrification mechanisms in soils (Delwiche, 1978). The current tropospheric mole fraction of N_2O is about 300 ppbv. Additional production of odd nitrogen is due to lightning in the troposphere and lower stratosphere, galactic cosmic rays near the tropopause, especially at high latitude, and precipitation of energetic particles during solar proton events (see Brasseur and Solomon, 1984 for a full discussion).

During the daytime, NO and NO_2 are closely coupled essentially through the following reactions involving ozone and atomic oxygen:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (1)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (2)$$

$$NO_2 + O \rightarrow NO + O_2. \qquad (3)$$
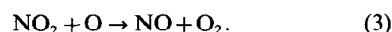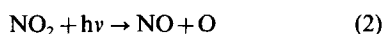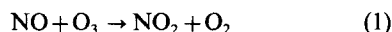
The characteristic time of this cycle being of the order of a few minutes in the stratosphere, equilibrium conditions between NO and NO_2 are reached almost instantaneously.

Nitrogen dioxide can also be converted in the presence of hydroxyl radicals (OH) into nitric acid (HNO_3)

$$NO_2 + OH + M \rightarrow HNO_3 + M. \qquad (4)$$

This molecule is destroyed by the two following reactions

$$HNO_3 + h\nu \rightarrow NO_2 + OH \qquad (5)$$

$$HNO_3 + OH \rightarrow NO_3 + H_2O \qquad (6)$$
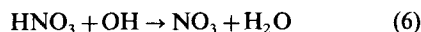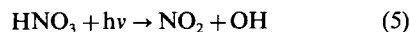
and, in the lower stratosphere and troposphere, by scavenging processes in water droplets. This process establishes an efficient wash-out mechanism of odd nitrogen from the stratosphere. The loss of nitric acid is, however, relatively slow so that the concentration of this compound is the highest of all odd nitrogen species in the lower stratosphere and its lifetime is of the order of weeks below 30 km. Much of the behavior of HNO_3 is thus controlled by dynamical processes on a variety of scales. Transport is, for example, responsible—at least in large part—for the latitudinal increase in the HNO_3 mixing ratio, which is prominent in winter.

During the night-time, when reactions (2)–(6) do

not occur, nitric oxide (NO) disappears during sunset and nitrogen dioxide (NO_2) is destroyed by

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{7}$$

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M. \tag{8}$$
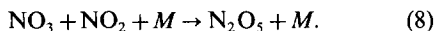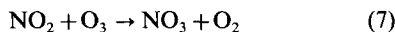
Nitrogen pentoxide (N_2O_5), which is expected to be a temporary reservoir of odd nitrogen in the stratosphere, is thus built up almost exclusively during the night-time since NO_3 is rapidly destroyed in the sunlit atmosphere. N_2O_5 is also photodissociated during the daytime:

$$N_2O_5 + h\nu \rightarrow NO_2 + NO_3$$
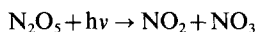
but with a time scale which is of the order of hours to days below 40 km. In the lower stratosphere, the concentration of this molecule never reaches its daytime equilibrium value, except in the polar regions where the length of the day in summer is considerably longer than 24 h. A diurnal variation of $NO_x = NO + NO_2$ is thus produced by the interchange between NO_2 and N_2O_5. In the polar night most of the NO_2 is converted into N_2O_5 so that large quantities of N_2O_5 and very small amounts of NO_2 should be observed during winter time in the polar cap (Knight et al., 1982; Solomon et al., 1984). A conversion of N_2O_5 to HNO_3 by reaction with aqueous aerosol has been proposed recently by Evans et al. (1985) and, if correct, could contribute to resolve the HNO_3 deficit found at high latitude in two-dimensional models (Ko et al., 1986; Austin et al., 1986). In the presence of large planetary waves in winter, air parcels with high N_2O_5 and low NO_2 concentrations can be transported from polar to midlatitude regions in a few days (Noxon, 1979; Solomon et al., 1984; Callis et al., 1983; Mount et al., 1984; Brasseur and Rose, 1985). Chemistry as well as dynamics thus plays an important role in establishing the distribution of active nitrogen species. It is therefore not surprising to observe considerable variability in the data obtained at different locations or at different times, especially in winter.

3. DIURNAL VARIATION OF NO_2 AND NO

Since NO and NO_2, which exhibit strong diurnal variations, have been measured during the MAP/GLOBUS campaign at different times of the day, it is necessary, in order to perform intercomparisons between data, to convert the observed values to a noontime concentration by applying to the measured NO or NO_2 amounts a conversion factor provided by a diurnal model. Moreover, a comparison between the observed and the calculated variations of the NO and NO_2 concentrations may help to understand odd nitrogen chemistry and will prove to be useful in constraining theoretical models. In fact the validation of the chemical scheme is most easily done by analyzing concentration ratios rather than absolute concentrations. This allows the large differences due to different treatments of transport processes which affect the amount of total odd nitrogen to be eliminated.

Figure 1 shows for different altitudes the concentration of NO_2 as a function of time (LLNL model). This concentration reaches a maximum at 25 km with a mixing ratio of about 3.2 ppbv at noon, 6 ppbv just after sunset, 4.6 ppbv at midnight and 3.2 ppbv just before sunrise. The sudden increase in NO_2 when the sun sets results from the fast conversion of NO to NO_2 through reaction (1) and the simultaneous interruption of reactions (2) and (3). The slow continuous decrease during the night is due to reaction (7) leading to the formation of N_2O_5. This last chemical process is principally visible at 25 and 30 km where the concentration of ozone is maximum. At sunrise, the concentration of NO_2 is rapidly reduced as reactions (2) and (3) reproduce NO. During the daytime, the amount of NO_2 (and NO) increases continuously as a result of the slow photodissociation of N_2O_5.

In order to convert MAP/GLOBUS 1983 data taken at different times of the day or the night to values corresponding, for example, to noon, the ratio of the NO_2 concentration to its value at noon has been calculated in the different models involved in the present study. A model intercomparison is first made, ignoring multiple scattering of solar light and reflection of the radiation at the Earth's surface or by the clouds in the troposphere. This ratio obtained for these simplified conditions is displayed as a function of time and for an altitude of 30 km in Fig. 2. Although the general qualitative waveform of NO_2 is similar in the different models, large quantitative differences appear. For example, the value of the ratio at midnight is 1.15 in the model of Schmailzl (MPI) and Brasseur (IAS), 1.19 in the model of Cariolle (Meteorologie Nationale), 1.2 in the model of Wuebbles (LLNL), 1.34 in the model of Pyle (Cambridge) and 1.58 in the model of Röth (Univ. of Essen). Part of these differences is due to the way the temperature dependence of the N_2O_5 absorption cross-section is treated and to the fact that, in most of these models, the ozone concentration is specified (2.8×10^{12} cm^{-3} at 30 km) while, in other models, it is calculated self-consistently with the other species (e.g. 3.5×10^{12} cm^{-3} at 30 km in the model of Brasseur). The ratio between the NO concentration to its value at noon, obtained with the same conditions as for NO_2, is shown in Fig. 3. The dispersion of the results is explained by the

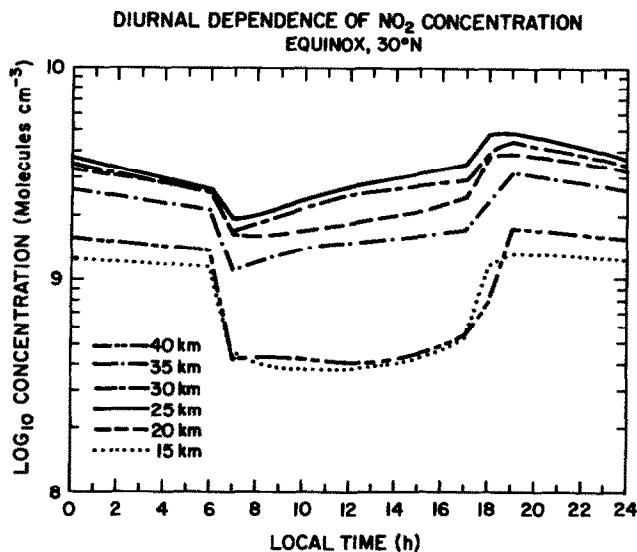DIURNAL DEPENDENCE OF NO₂ CONCENTRATION
EQUINOX, 30°N

FIG. 1. DIURNAL DEPENDENCE OF THE NO₂ CONCENTRATION CALCULATED AT SELECTED ALTITUDES, 30°N
AND EQUINOX (LNLL MODEL).
Albedo (0.3) and multiple scattering are considered.

same causes as for NO_2. The decrease of the NO density, several hours before sunset, apparent for example in the data obtained during the MAP/GLOBUS 1983 campaign by Kondo et al. (1985), may be explained by an increase in the optical depth for the radiation involved in the photodissociation of NO_2. An accurate determination of the photolysis rate of nitrogen dioxide (J_{NO_2}) for large zenith angles indeed requires one to consider a full spherical geometry as well as the effects of albedo and multiple scattering by both molecules and aerosols (see e.g. Madronich et al., 1985). Mugnai et al. (1979) have, for example, indicated that a significant part of the optical depth in the spectral range where NO_2 photodissociates, may be due to the attenuation by aerosols (not considered in the present study). The variation with time of the NO and NO_2 densities near sunset or sunrise are thus sensitive to the aerosol load of the atmosphere, especially after large volcanic eruptions such as El Chichon.

The effect of multiple (Rayleigh) scattering and albedo on the $[NO_2]/[NO_2]_{noon}$ ratio at 30 km can be estimated from Fig. 4 (model of Pyle). The maximum amplitude of this ratio is significantly increased and is expected to be even larger over regions where the albedo is higher. Furthermore, the slope of the daytime NO_2 variation is also increased since multiple scattering and albedo also affects the photodissociation of N_2O_5. The curve corresponding to $A = 0.3$ should be used for the interpretation of the MAP/GLOBUS data since the average albedo during

the campaign was close to 30% (Pommerau, personal communication). It is interesting to note that the ratio between $[NO_2]$ immediately after sunset and $[NO_2]$ for a low zenith angle, as derived from the LIMS data by Solomon and Russell (1986), is equal to 2.5 at 10 mb and 2.2 at 16 mb. The theoretical value obtained by Pyle at 30 km (12 mb) for the $[NO_2]_{sunset}/[NO_2]_{noon}$ ratio is less than 1.7 when scattering and albedo are neglected and 2.1 when those effects are taken into account. This emphasizes the importance of multiple scattering and albedo in the determination of the concentration of nitrogen oxides. Therefore the concentration of odd nitrogen species is expected to be variable not only because of transport processes but also due to the geographic variations in the albedo (e.g. effects of vegetation, presence of clouds).

4. COMPARISON BETWEEN OBSERVED AND CALCULATED PROFILES

The NO_x data as well as the uncertainty in the measurements are discussed in several papers appearing in the present issue (see e.g. Pommerau et al., 1987 for instrument description and data comparison). The consistency of the observed concentrations with the currently accepted stratospheric chemistry is now tested by comparing selected observed vertical distributions of active nitrogen species with profiles calculated by several of the 1-D models involved in the present study. This type of comparison can only lead to very partial results as the models predict average
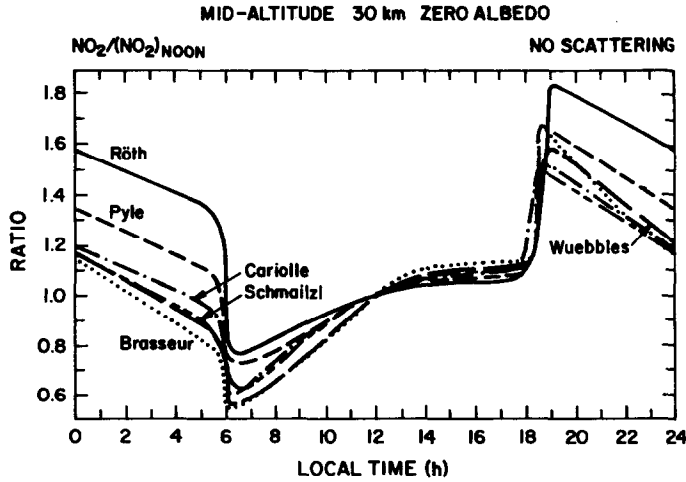
MID-ALTITUDE 30 km ZERO ALBEDO

$NO_2/(NO_2)_{NOON}$ NO SCATTERING

FIG. 2. DIURNAL DEPENDENCE AT 30 km ALTITUDE OF THE RATIO OF THE NO_2 CONCENTRATION TO ITS VALUE
AT NOON CALCULATED BY DIFFERENT MODELS INVOLVED IN THE PRESENT STUDY.
Multiple scattering and albedo are not considered.

MID-LATITUDE 30 km ZERO ALBEDO
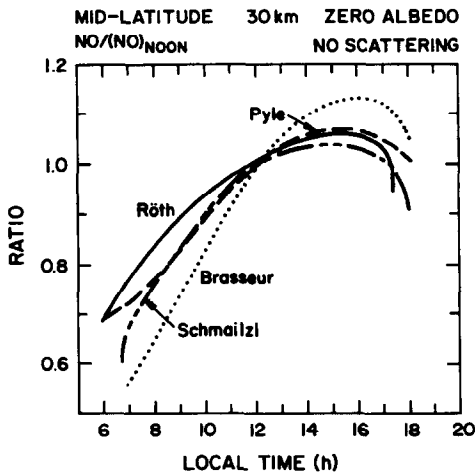$NO/(NO)_{NOON}$ NO SCATTERING

FIG. 3. SAME AS FIG. 2, BUT FOR NO.

values while the observations may reflect special conditions with sporadic dynamical effects. It should also be kept in mind that the different models may produce somewhat different results as the various inputs such as the transport representation, the boundary conditions, etc. are not necessarily the same in all models. For example, the calculated mixing ratio of total odd nitrogen is sensitive to the choice of the eddy diffusion coefficient. Moreover, it should be noted that one-dimensional models tend to predict somewhat lower concentrations of total odd nitrogen than two-dimensional models (Solomon, personal communication). Such differences arise from the fact that 1-D models calculate the production rate of odd nitrogen from a mid-latitude N_2O profile, quickly declining with alti

tude, while 2-D models use essentially the much slower declining N_2O profile in the tropics, as most of the active nitrogen is produced in this region.

Figure 5 compares the NO mixing ratio measured by Kondo et al. (1985) and by Fabian et al. (1987) (20 September 1983) with the corresponding profiles calculated by the models of Schmailzl and of Brasseur. The agreement is generally good, especially in the layer between 22 and 27 km altitude. Near the tropopause as well as above 28 km, the reported mixing ratios are higher than the calculated values. This difference is consistent with an underestimation by the models of the total odd nitrogen amount. At lower altitude, it might reflect intrusion of tropospheric air.

The vertical distribution of the NO_2 mixing ratio measured during daytime by Helten et al. (1985) (9 September 1983), Fabian et al. (1987) (20 September 1983) and by the Solar Mesosphere Explorer over Europe (Naudet et al., 1987) is compared in Fig. 6 to the theoretical profile calculated from the IAS model (Brasseur), from the LLNL model (Wuebbles) and from the model of the Meteorologie Nationale (Cariolle) for noon conditions. The overall shapes of the theoretical and observed profiles are very similar but differences in the mixing ratios may be large at certain altitudes. On average the calculated values are somewhat higher than the concentrations measured by Helten et al. and by Fabian et al. during the descent of the balloon but lower than the values obtained by Fabian during the ascent part of the flight. The model results also fall in the uncertainty limits (not represented) of the SME values. NO_2 mixing ratios calculated by the same models of Wuebbles, Brasseur
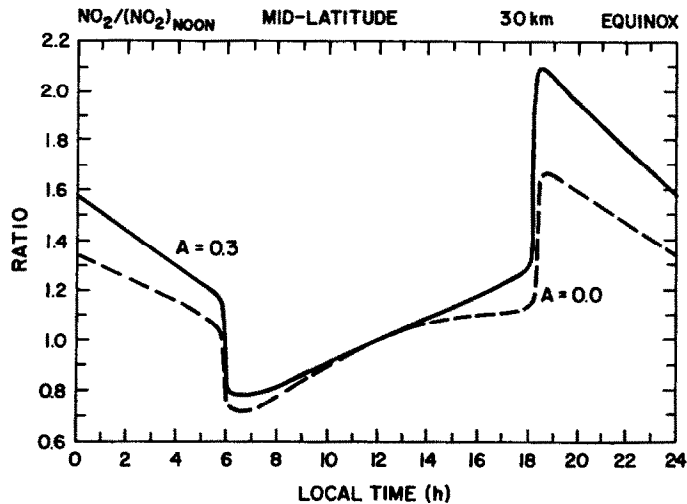
FIG. 4. EFFECT OF MULTIPLE SCATTERING AND ALBEDO (= 0.3) ON THE CALCULATED DIURNAL VARIATION OF THE NO_2 CONCENTRATION.
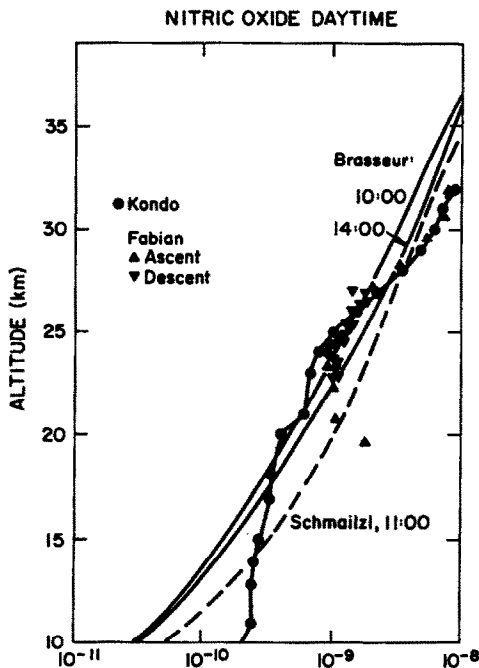The values are expressed relative to the concentration at noon (model of Pyle).

FIG. 5. VERTICAL DISTRIBUTION OF THE NO MIXING RATIO DURING DAYTIME.
Comparison between observed values (Kondo; Fabian) and calculated profiles (Schmailzl; Brasseur).

and Cariolle for night conditions are compared in Fig. 7 to the observations also made during the night. The agreement between theory and measured data reported by Offermann et al. (1987) (23 September 1983) and Rigaud and Naudet (personal communication, 1986) (14 September 1983) is excellent near 35 km. At 32 km, the calculated relative concentrations are close but somewhat lower than the value given by Offermann et al. and significantly higher than the mixing ratio provided by Helten et al. (1985) (9 September 1983). Near 30 km, the observation of Offermann et al. is a factor 1.5–2 higher than the model prediction.

The night-time NO_3 mixing ratios measured by Rigaud and Naudet (personal communication, 1986) (14 September 1983) and by Helten et al. (1985) (20 September 1983) are compared to the vertical distributions calculated by Röth and by Cariolle (Fig. 8). The agreement between the data of Rigaud and Naudet (personal communication, 1986) and the models is excellent but the mixing ratios reported by Helten et al. are a factor 2 larger than the theoretical calculation.

Finally, the HNO_3 mixing ratio measured by Offermann et al. (1987) (23 September 1983) is compared to a 24-h averaged profile taken from the model of Brasseur (Fig. 9). The agreement between the model and the observations is good. One should nevertheless remember that the data by Offermann et al. are higher than most other measurements obtained in the upper stratosphere by balloon-borne instruments (see WMO/NASA, 1987) and that most models tend to overestimate the HNO_3 concentration by a factor of 1.5–2 compared with these observations. Unless an important mechanism is omitted, this overestimation of the predicted HNO_3 concentration may be related,
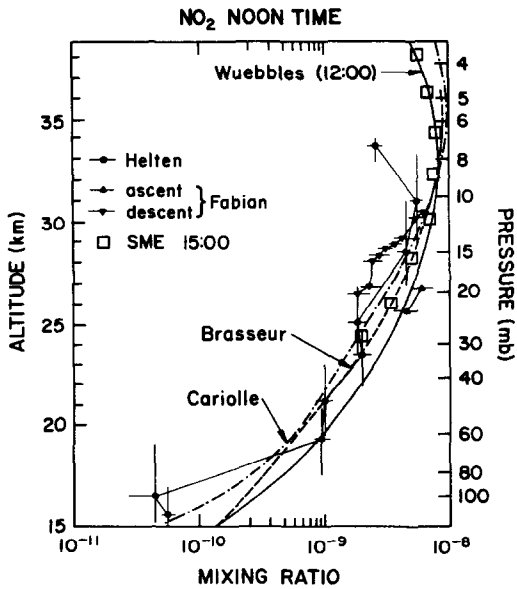
FIG. 6. VERTICAL DISTRIBUTION OF THE NO_2 MIXING RATIO DURING NOONTIME.

Comparison between observed values (Helten; Fabian; Naudet *et al.*, 1987) and calculated profiles (Wuebbles; Cariolle; Brasseur).
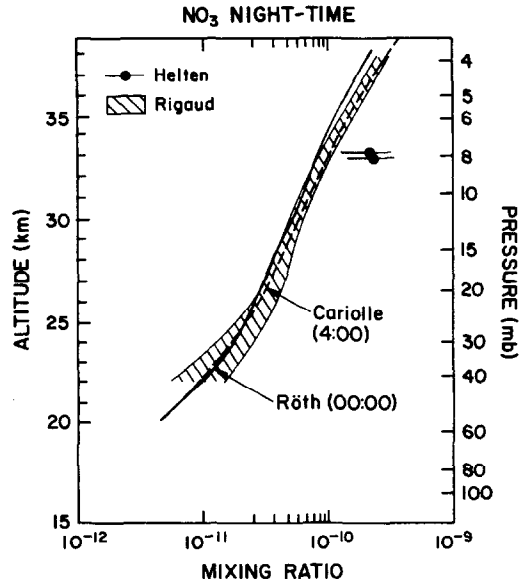

FIG. 8. VERTICAL DISTRIBUTION OF THE NO_3 MIXING RATIO DURING THE NIGHT-TIME.

Comparison between observed values (Rigaud; Helten) and calculated profiles (Röth; Cariolle).
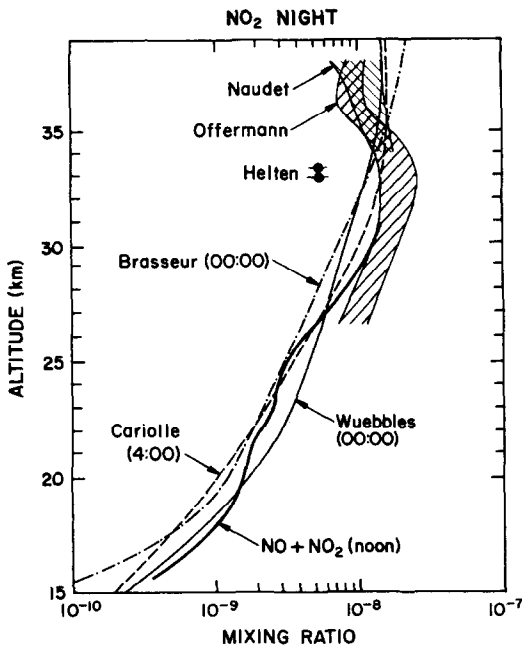

FIG. 7. VERTICAL DISTRIBUTION OF THE NO_2 MIXING RATIO DURING THE NIGHT-TIME.

Comparison between observed values (Helten; Rigaud; Offermann) and calculated profiles (Wuebbles; Cariolle; Brasseur). The total concentration of NO and NO_2 based on daytime measurements is also indicated (see Pommerau *et al.*, 1987).
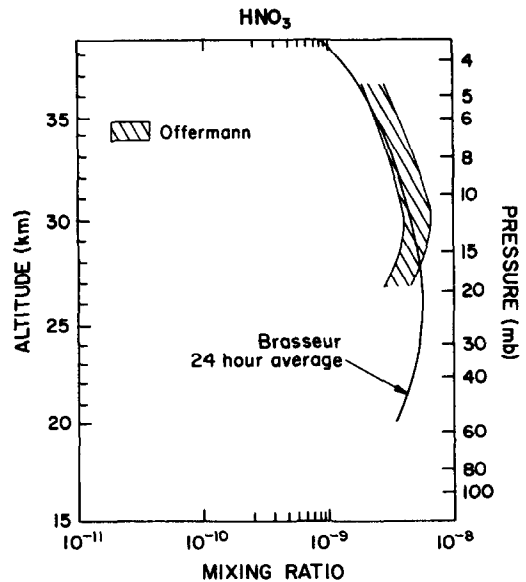

FIG. 9. COMPARISON BETWEEN THE VERTICAL DISTRIBUTION OF NITRIC ACID MEASURED BY OFFERMANN AND PROVIDED BY THE MODEL OF BRASSEUR.

for example, to an improper calculation of the solar transmission in the spectral region of the Schumann–Runge bands.

5. SUMMARY

As the total number of active nitrogen is fairly well conserved in the middle atmosphere, the concentration of odd nitrogen, especially during dynamically disturbed conditions, is highly variable with transport processes. Variations are expected to appear in the observed concentrations of nitrogen oxides during the MAP/GLOBUS campaign, especially if wavelike disturbances were present during this period (Offermann et al., 1987). Therefore, as models predict only average values for a particular time of the year, the comparison between observed and calculated NO, NO_2, NO_3, HNO_3, etc. is not straightforward. Most vertical distributions of these species observed during the campaign seem, however, to be consistent with the chemical scheme currently used in photochemical models. The discrepancy between observed and calculated HNO_3 in the upper stratosphere cannot be resolved as the number of observations of this species during the campaign was very limited.

The concentration of the individual species belonging to the odd nitrogen family varies significantly during the day, as a result of a radically different chemistry between day and night. These types of changes are simulated by all models involved in the present study, but with significant quantitative differences. Rapid changes in the concentration of most nitrogen species occur at sunrise and sunset as stratospheric NO is only present in the sunlit atmosphere. The rapid disappearance of nitric oxide at sunset, previously noticed by Ridley et al. (1977) and others, has been observed during the campaign by Kondo et al. (1985). Changes in the concentration of nitrogen oxides at a much slower rate occur both during the night and the day as a result of the formation and destruction of N_2O_5. No continuous observation of NO_2 is available from this campaign to confirm the importance of N_2O_5 in the chemistry of odd nitrogen in the stratosphere. Evidence for the transformation of NO_2 into N_2O_5 during the night appears, however, in the measurements of Knight et al. (1982) and in the analysis of the high latitude summer data analyzed by Solomon and Russell (1986). It is expected that future campaigns will provide additional information, which will be useful to validate the currently accepted photochemical scheme of active nitrogen in the stratosphere.

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