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DIURNAL VARIATION OF NITRIC OXIDE AT 26 km

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Abstract. A chemiluminescent NO detector was launched from Uchinoura, Japan (31°N), at 0030 JST on July 29, 1987. The balloon reached a float altitude of 26 km at around 0200 JST and stayed at this altitude until 1600 JST when it started a slow descent. Near local sunrise, when the solar zenith angle reached 92.7°, the NO concentration started to increase rapidly. This rapid increase continued for about 30 minutes. The NO concentration continued to increase, albeit more slowly, for a further 7 to 8 hours, and then became stable. The NO diurnal variation is calculated by a time-dependent photochemical model assuming a 14 ppbv total odd nitrogen concentration, constrained by ozone and temperature measured simultaneously with NO; the result agrees quite well with the observed temporal NO variation. The observed slow increase in NO can quantitatively be explained by the photodissociation of N_2O_5. The N_2O_5 concentration just before sunset is estimated to be 1.9 ±0.4 ppbv at 26 km.

Introduction

Nitric oxide in the lower stratosphere predicted by current photochemical models undergoes a large diurnal variation [e.g., Ko and Sze, 1984; Brasseur et al., 1987]. The variation of NO after sunrise is caused by the photodissociation of both NO_2 and the reservoir species, mainly N_2O_5, formed during the night. The time constant of the photodissociation of NO_2 during the day is of the order of a few minutes, while in the lower stratosphere that of N_2O_5 is of the order of several hours. This is due to the fact that N_2O_5 is photodissociated mainly by solar ultraviolet radiation between 200 and 300 nm, which is strongly absorbed by ozone. In this way, important photochemical processes, such as the production and photodissociation of reservoir species, are involved in the diurnal variation of NO and NO_2. Consequently, the measurement of the diurnal variation of NO should lead to an understanding of these basic photochemical processes. The temporal variation of NO in the lower stratosphere near sunrise has been measured in detail by Ridley et al. [1977]. Temporal variations at higher altitudes have also been reported [e.g., Roscoe et al., 1986; Kondo et al., 1988, 1989]. Since the time constant of the photodissociation of N_2O_5 grows larger with decreasing altitude, the measurement of the diurnal variation of NO for as long as possible during the sunlit hours will lead to a more complete understanding of the photochemistry of the oxides of nitrogen in this region. For this reason, a balloon-borne measurement of NO was made at an altitude of 26 km on July 29, 1987. Measurements of NO were made for about 12 hours from sunrise. The balloon flew from Japan to China across the East China Sea, providing detailed information on the diurnal variation of NO.

Instrumentation

Detailed descriptions of the chemiluminescent NO detector used for the balloon observation are given in Kondo et al. [1984, 1988, 1989]. To measure the zero level of the instrument, purified air was injected for 40 s every 10 minutes upstream of the reaction chamber with mass flow rates twice as large as those of the sample air. To obtain a more precise estimate of the sample flow rate, a systematic calibration has been performed in the laboratory. Recently we have found that the sensitivity of the mass flow sensors used to control the calibration NO gas and the ozone/oxygen mixture gas increases with the decrease in the ambient pressure [Kondo et al., 1989]. This effect was more important for the mass flow controllers used for the present experiment (STEC, SEC-421 MK II) than for that used in our previous experiments (Tylan FC-260) [Kondo et al., 1984, 1985, 1988]. This effect has been taken into account, as described in Kondo et al. [1989], in deriving the NO mixing ratios reported here. As far as the present experiment is concerned, the fluctuation of the zero level was unusually high and this made the precision of the measurement about 0.1 ppbv, compared to approximately 0.02 ppbv for previous experiments.

Two essentially identical radiometers were mounted on the balloon gondola in order to measure the upward and downward radiation. The top of each radiometer was covered with a plastic hemispherical shell to diffuse incoming radiation. The diffused radiation is passed through an interference filter with a center wavelength of 420 nm and a half width of 14 nm and then detected by a phototube (Hamamatsu R727). The sensitivity of the radiometer changes almost linearly with the angle of incidence of the incoming radiation. The sensitivity of the two radiometers was adjusted to be equal using the sun as a light source. The radiometers were mounted about 80 cm out from the NO instrument, which has dimensions of 120(L) x 90(W) x 90 (H) cm.

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Ozone was measured on board the gondola with a potassium-bromide-iodide (KBr-KI) electrochemical ozone sonde (Meisei Electric, RS II-KC78), which is used for routine balloon measurements in Japan. Simultaneous measurements of ozone were also performed by the BUV instrument on board the Japanese satellite EXOS-C [Suzuki et al., 1985]. With this instrument ozone profiles can be derived from the measurement of the backscattered solar radiation in the wavelength region between 250 and 320 nm.

Results

The gondola for NO and ozone instruments was suspended about 20 m below a 15,000 m^3 balloon and launched from Uchinoura, Japan (31°N, 131°N), at 0030 JST on July 29, 1987. The balloon reached a float altitude of 26 km (21±1 mb) around 0200 JST and stayed at this altitude until 1600 JST when it started a slow descent. The balloon moved westward from 131°E to 120°E at a speed of about 0.7°longitude/hour. It stayed in the latitude range of between 31 and 32°N throughout the flight. Most of the NO measurements were made over the East China Sea. Photographs taken from the meteorological satellite show that the balloon flight area was either cloud-free or covered only by very narrow bands of clouds.

The profiles of ozone measured by the ozonesonde and the BUV instrument are shown in Figure 1. The BUV measurement was made at 33.0°N and 132°E at 0812 JST on July 29. It can be seen that both measurements agree quite well between 23.5 and 26.5 km. The temperature measured on board the balloon indicated that the altitude and temperature of the tropopause were 15.5 km and -76°C, respectively. The temperature measured at the float altitude was -49°C.

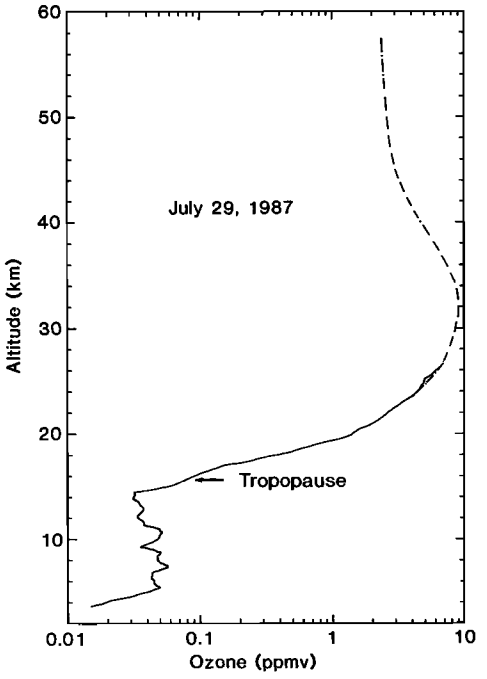

Fig. 1. Ozone profiles measured by a ozonesonde (solid line) and by the BUV instrument (dash-dotted line). The arrow indicates the position of the tropopause.

The NO mixing ratio measured at the float altitude is shown in Figure 2. It can be seen that a rapid increase in NO starts at about 0530 JST when the solar zenith angle reaches 92.7°. This rapid change in NO continues for 20 to 30 minutes. Thereafter, NO continues to increase, but more slowly. These features near sunrise are quite similar to those measured previously at 26.5 km [Ridley et al., 1977] and at 32 km [Kondo et al., 1988, 1989]. The increase observed at 26 km seemed to continue until around 1400 JST. The NO concentration between 1400 and 1630 JST is nearly constant at 2.05±0.15 ppbv. This daytime NO concentration is 2.5 to 3 times larger than that at 0600 JST. As will be discussed later, this slow increase that continued for 7 to 8 hours can be explained by the photodissociation of N_2O_5. The decrease in NO observed after 1645 JST is due to the slow descent of the balloon.

The signals from the upward- and downward-looking radiometers are shown in Figure 2. Small-scale variations in the signal are due to the change in the orientation of the NO instrument relative to the sun. As can be seen from Figure 2, the gondola was in the shadow of the balloon between 1145 and 1400 JST. From a calculation taking into account the geometry of the balloon and the gondola, it was expected that the sun as seen from the gondola would be masked by the balloon during this time. The small increase in the upward radiation around 1030 and 1400 JST is due to the small clouds seen in the satellite photographs. Unfortunately uncertainties in NO measurement of about 0.1 ppbv make it difficult to separate out the possible effect of the irregular variation in the radiation on the NO concentration.

Model calculation

The diurnal variation of NO at 26 km at the same latitude and on the same day of the year as the balloon observation described above has been calculated by using a time-dependent zero-dimensional model described by Pirre et al. [1989]. The photodissociation coefficient of NO_2 used in this model is very close to the one computed by Madronich et al. [1985] for an altitude of 24 km using a low albedo of 0.15. The photodissociation coefficient of N_2O_5 has been computed by taking into account the absorption cross section measured by Yao et al. [1982] and the temperature measured at the float altitude. Other reaction rate coefficients have been adopted from JPL [1987] for the measured temperature. By fixing the concentration of the total oxides of nitrogen (NO_y = NO + NO_2 + NO_3 + $2N_2O_5$ + HNO_3 + $ClONO_2$ + HO_2NO_2) at 26 km, the temporal variations of short-lived species such as NO, NO_2, and N_2O_5 can be calculated. For this calculation, the measured ozone profile, as shown in Figure 1, was used. The NO_y concentration encountered during the flight should have changed little as the balloon moved westward staying within the same air parcel. $ClONO_2$ is calculated to undergo little diurnal variation and hence is not discussed here. The calculated NO concentration as a function of local time for NO_y values of 13, 14, and 15 ppbv, are shown in Figure 3 together with

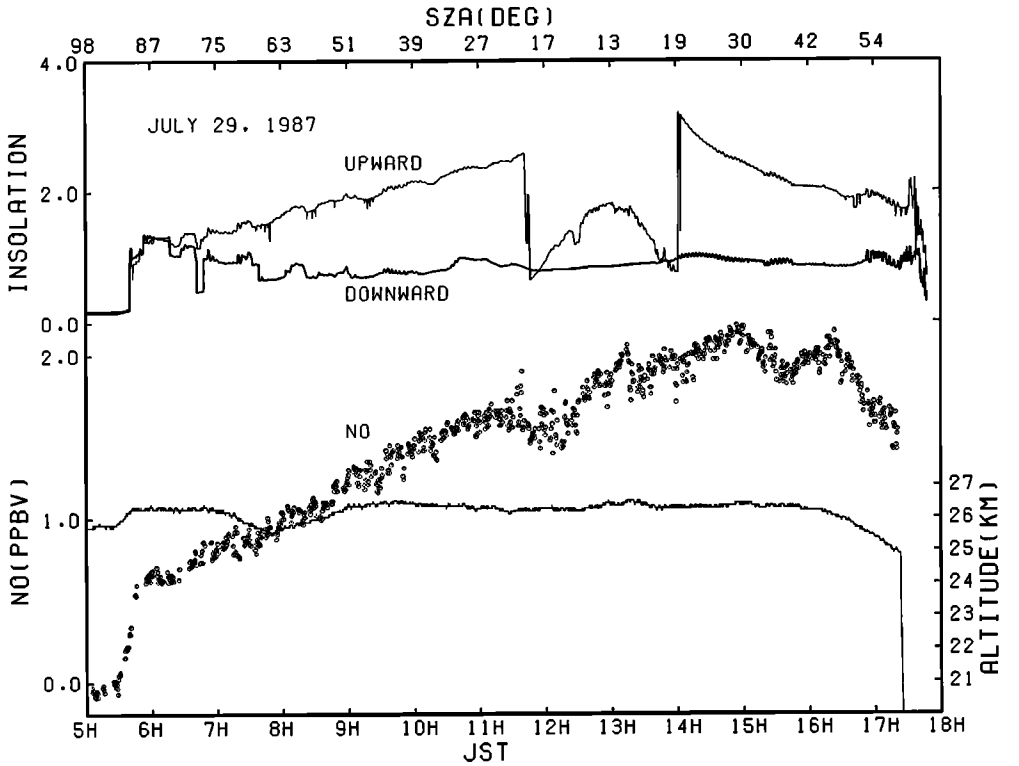

Fig. 2. Observed NO mixing ratio at the float altitude as a function of Japanese Standard Time (JST). Upward and downward radiation intensities and the altitude of the balloon are also shown. The solar zenith angle is given in degrees.

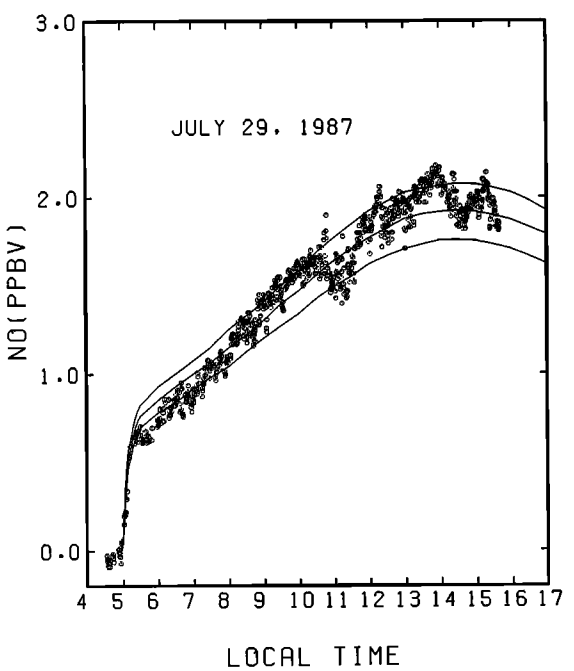

Fig. 3. Comparison of the observed (circles) and the computed values (solid lines) of NO concentration versus local time. NO data obtained after 1645 JST (1540 local time) are eliminated for clarity. Computed curves are for NO_y values of 13 ppbv (bottom curve), 14 ppbv, and 15 ppbv (top curve).

the measured values. Here the local time (LT) is defined as

$$LT\ (hour) = JST\ (hour) - 0.1079 + [Longitude(deg) - 135]/15.$$

The NO values observed after 1645 JST (1540 LT) are excluded in this figure for clarity. Considering that the precision of the NO measurement is 0.1 ppbv, the agreement between the calculation and the measurement is very good, especially for the flattening of the NO curve around 1400 LT.

In order to look in detail at the partitioning of the NO_y species, the calculated diurnal variations of NO, NO_2, N_2O_5, and HNO_3, for the 14 ppbv of NO_y, are shown in Figure 4. The NO_2 concentration at noon of 3.3 ppbv is in agreement with the observations compiled in WMO [1986]. The N_2O_5 concentration is calculated to be 1.9 ppbv at the end of the night and decreases to 0.55 ppbv at the end of the daytime. The nighttime value is within the error bar of the recent measurement by Kunde et al. [1988] but is a factor of 3 larger than the value measured by Toon et al. [1986]. HNO_3 is found to be nearly constant, as expected from its lifetime of about 10 days. The computed mixing ratio of 5.6 ppbv for HNO_3 is in the range of the other observed values of 5 to 6 ppbv, as compiled in WMO [1986], although the measured HNO_3 may not necessarily be in photochemical equilibrium with the rest of the NO_y family. In this way, the model not only reproduces the observed diurnal variation of NO but also gives concentrations of NO_2 and HNO_3 consistent with the existing measurements. In

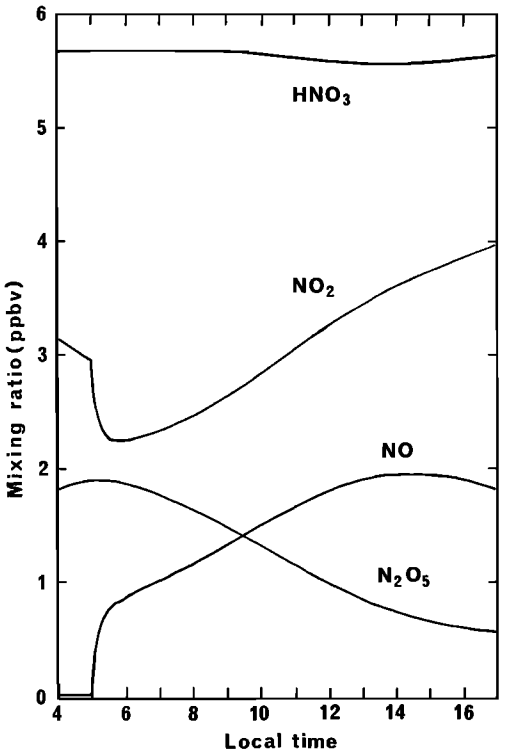

Fig. 4. Computed diurnal variations of NO, NO_2, N_2O_5, and HNO_3 for an NO_y value of 14 ppbv.

turn, the N_2O_5 concentration of 1.9 ppbv with an uncertainty of ±20% is a reasonable estimate for the amount of N_2O_5 under the observational conditions on this particular day.

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