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# Altitude Profile and Sunset Decay Measurements of Stratospheric Nitric Oxide

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[Manuscript received 11 February 1976; in revised form 24 March 1976]

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## ABSTRACT

In July 1974 an  $NO/O_3$  chemiluminescent instrument was used to obtain measurements of  $NO$  in the stratosphere during two balloon flights launched from Churchill ( $59^\circ N$ ,  $95^\circ W$ ). On the first flight, an altitude profile was obtained in which the  $NO$  volume mixing ratio was observed to increase from 0.3 to 2.7 ppbv between 19 and 29.5 km. On the second flight, the mixing ratio

was observed to increase from 0.25 to 2.7 ppbv between 19 and 29 km and to remain almost constant at about 2.7 ppbv from 29 to 34.5 km. On this flight, the sunset decay of  $NO$  was also obtained while the payload was at a constant float altitude of 34.5 km. These decay measurements are compared satisfactorily with the results obtained from a time dependent stratospheric model.

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## 1 Introduction

The measurement of  $NO$  altitude profiles in the stratosphere provides an important means of assessing photochemical dynamical stratospheric models used to estimate the effect of anthropogenic perturbations on  $O_3$ . However, the altitude profiles of a minor constituent such as  $NO$  depend on a complex interaction of chemistry and dynamics. Since most models parameterize dynamics with a single parameter, the eddy-diffusion coefficient, and use average insolation conditions because of the large differences in most chemical and flow time constants, agreement between measurement and theory cannot be expected to be very exact. Thus one ought to explore other methods of validating the models. One such method is to measure the diurnal variation dependence at a given location and altitude. Diurnal changes for  $NO$  occur on a much shorter time-scale than most atmospheric motions so that a test of agreement between models and measurement will be a test of specific chemistry uncomplicated by serious dynamic influences.

In this paper we present  $NO$  measurements which allow both of the above types of assessments to be made. *In-situ* measurements of the height profiles of  $NO$  and the first measurement of the change in  $NO$  concentration at a constant altitude through sunset are presented. Due to the apparent variability of  $NO$  profiles measured, no theoretical comparison is made since the models used to date cannot simulate such short-term profile variability. However the constant-altitude sunset data are compared with a time-dependent model calculation.

Simultaneous measurements of  $NO$ ,  $NO_2$ ,  $HNO_3$  and  $O_3$  also provide a means to check models. Such measurements were also made during one of the flights described herein. An intercomparison of these results is given in another paper in this issue (Evans *et al.*, 1976).

## 2 Experimental

The  $NO/O_3$  chemiluminescent instrument for *in-situ*  $NO$  sampling has been described in detail by Ridley and Howlett (1974). Experimental tests in the laboratory and during balloon flights to confirm the absence of sampling errors with the payload configuration used here have also been described (Ridley *et al.*, 1975a). Provision is made for on-board calibration of the instrument by the periodic addition of small known flows of  $NO$  to the ambient air flow from a high pressure cylinder containing a few ppm of  $NO$  in  $N_2$ . Analysis of this flight cylinder by comparison with laboratory standards just before and after the balloon flights gave results which agreed to 5%. The estimated accuracy of the data presented below is  $\pm 30\%$ .

The balloons were launched from Churchill,  $59^\circ N$ ,  $95^\circ W$ . Flight 1 occurred on 16 July 1974, using a  $2.3 \times 10^4$  m<sup>3</sup> balloon with the payload suspended some 30 m below. Measurements were made between 1700 and 2000 LT during ascent and float. Flight 2 occurred on 22 July 1974 using a  $3.1 \times 10^5$  m<sup>3</sup> balloon with the payload suspended about 100 m below. Measurements of the  $NO$  altitude profile and decay during sunset were made between 1930 and 2310 LT. Visible sunset occurred near 2308 LT. For Flight 2 there is an uncertainty of  $\pm 0.5$  km in the float altitude of the payload. Below about 29 km the uncertainty is much less.

## 3 Results

The  $NO$  mixing ratios obtained for solar zenith angles,  $\chi$ , less than  $90^\circ$  are shown in Fig. 1. The corresponding number densities tabulated in Tables 1 and 2 were calculated from the mixing ratios using atmospheric data provided from radiosondes released from the Churchill Meteorological Station. The  $O_3$  and temperature profiles shown in Fig. 2 were obtained from an ozonesonde released directly after the  $NO$  experiment was launched.  $O_3$ , temperature and weather information for Flight 2 are reported by Bain *et al.*, (1976). The tropopause altitudes for flights 1 and 2 were both approximately 11 km.

For both flights, the  $NO$  mixing ratio increases quite strongly between about 19 and 29 km, a trend in agreement with earlier flights from New Mexico (Ridley *et al.*, 1975a). Flight 1 exhibits significantly higher mixing ratios between 20 and 28 km, though the two profiles converge at higher altitude. When  $\chi \leq 90^\circ$ , on either flight, there is little variation in the measured mixing ratio during the float duration. Over the nearly 2-h float period of Flight 1, the box in Fig. 1 indicates the extremes determined, whereas the average  $NO$  mixing ratio was  $2.7 \pm 0.2$  ppbv. For Flight 2, the  $\chi \leq 90^\circ$  measurement period was much shorter ( $\sim 25$  min) but the average was again  $2.7 \pm 0.2$  ppbv.

During the float period of Flight 2, measurements of  $NO$  were made through

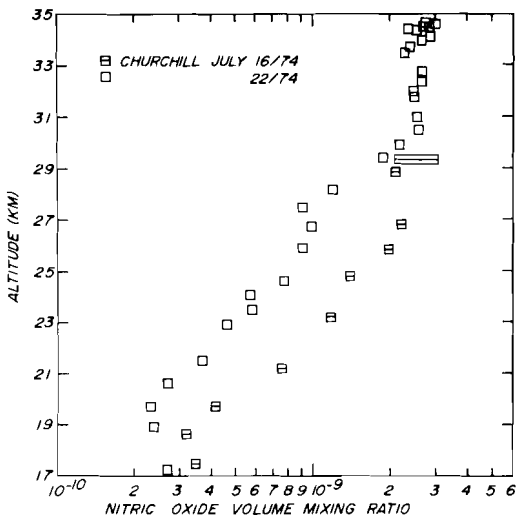
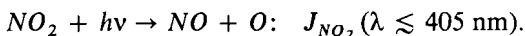
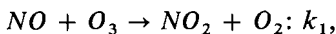


Fig. 1 High-sun  $NO$  mixing-ratio altitude-profiles obtained during the two balloon flights.

sunset. The open circles of Fig. 5 show the decay of  $NO$ , expressed as the ratio of  $NO$  during sunset to the average high sun ( $\chi \leq 90^\circ$ ) value of 2.7 ppbv. The instrument operated for an additional 2.5 hours after visible sunset until the coolant and  $O_3$  supplies were depleted but the  $NO$  mixing ratio remained below the detection limit of the instrument at this altitude ( $\sim 0.06$  ppbv). This confirms the expected absence of  $NO$  during night-time conditions.

#### 4 Discussion

The principal reactions which govern the interconversion of  $NO_2$  and  $NO$  are:



In the day-time stratosphere, the characteristic time-constant for the attainment of steady-state conditions is of the order of a few minutes, depending on the  $O_3$  concentration and temperature, while the characteristic time constant for macro-transport is much longer. Consequently, the photochemical steady-state condition should be valid and

$$\frac{[NO_2]}{[NO]} = \frac{k_1[O_3]}{J_{NO_2} + k_2[O]}. \quad (1)$$

Since both the photolysis coefficient,  $J_{NO_2}$ , and  $[O]$  decrease to zero in the absence of sunlight, this simple mechanism predicts conversion of  $NO$  to  $NO_2$  at sunset and re-appearance of  $NO$  at sunrise. The decay of  $NO$  into  $NO_2$  at sunset involves two time constants: (1) the time constant for conversion of  $NO$  into  $NO_2$ ,  $t_1 = 1/k_1[O_3]$  and (2) the time constant for change of  $NO_2$  into

TABLE 1. Nitric oxide data for flight of 16 July 1974

Altitude (km)	Number Density ( $\text{cm}^{-3}$ )
17.5	$9.4 \times 10^8$
18.6	7.2
19.6	8.2
21.2	11.0
23.2	13.0
24.8	12.0
25.8	15.0
26.8	14.9
28.8	11.0
$29.4 \pm 0.3$	$13 \pm 1^*$

\*average of 25 measurement cycles

TABLE 2. High-sun nitric oxide data for flight of 22 July 1974

Altitude (km)	Number Density ( $\text{cm}^{-3}$ )	Altitude (km)	Number Density ( $\text{cm}^{-3}$ )
17.2	$7.9 \times 10^8$	30.5	$9.7 \times 10^8$
18.9	5.5	31.0	9.1
19.7	4.6	31.8	7.7
20.6	4.7	32.0	7.5
21.5	5.6	32.4	7.6
22.9	5.6	32.8	7.1
23.5	6.4	33.5	5.4
24.1	5.8	33.7	5.5
24.6	7.1	34.0	5.9
25.9	7.0	34.1	6.0
26.7	6.7	34.4	5.3
27.5	5.4	34.4	4.9
28.2	6.5	34.5	5.7
29.4	8.5	34.5	5.7
29.9	9.1	34.6	6.0
		34.6	5.6

$NO$ ,  $t_2 = 1/(J_{NO_2} + k_2[O])$ . At sunset, if  $t_1$  is of order a few minutes, then as  $t_2$  (initially 2 minutes) becomes longer  $NO$  decreases, but because  $t_1$  is still short  $NO$  and  $NO_2$  remain in quasi-photochemical-steady-state and the decay is determined essentially by the time constant  $t_2$ . However if  $t_1$  is much longer than  $t_2$  (e.g.,  $t_1 = 40$  min at 50 km) then much of  $NO$  will survive well-past sunset and the decay will depend only on  $t_1$ , i.e., temperature and  $[O_3]$ .

The time constant  $t_2$  is determined mainly by UV solar flux so that  $t_2$  starts to increase before visible sunset.

## 5 Comparison of altitude profile data

Fig. 3 compares the high-sun Churchill data with measurements obtained during several flights from Holloman Air Force Base, New Mexico (Ridley

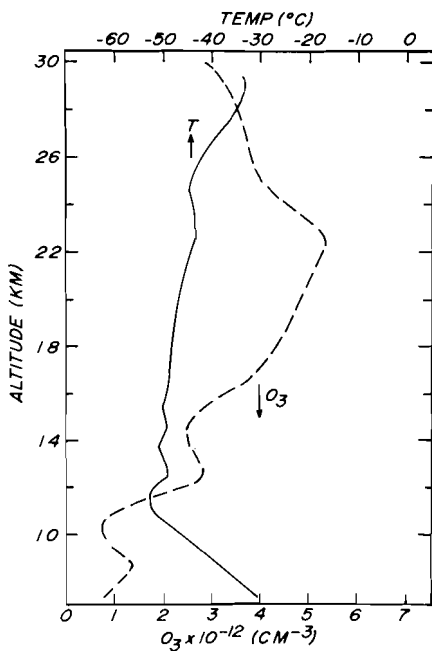


Fig. 2 Temperature and  $O_3$  data for the flight of 16 July (Flight 1).

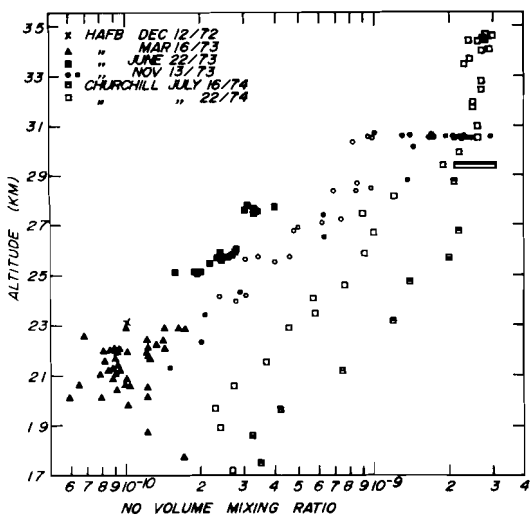


Fig. 3 Comparison of mixing-ratio altitude-profile data for Churchill and Holloman Air Force Base, New Mexico, balloon flights.

*et al.*, 1975a). All of the New Mexico data were obtained during the morning after UV sunrise on the payload using either of two essentially identical instruments. Although the altitude profiles exhibit similar trends of increasing mixing ratio with altitude between about 20 and 30 km there are extreme differences in the measured mixing ratios of up to an order of magnitude in the 21–27-km region. These differences are in excess of the estimated inaccuracy of each particular experiment. Eq. (1) illustrates that the partitioning of  $NO_x$  into  $NO$  and  $NO_2$  is quite sensitive to temperature through  $k_1$  and to the  $O_3$  density and a detailed analysis of all of the data to allow for these differences and the changes in  $J_{NO_2}$  will be reported at a later time. However, a qualitative comparison of just the ozone and temperature profiles for the Churchill flights and the New Mexico flights indicates that these factors cannot produce the order of magnitude change observed experimentally.

Loewenstein *et al.* (1975, 1976) have made a series of  $NO$  measurements from a high-altitude aircraft at 18.3 and 21.3 km to investigate both the seasonal and latitudinal dependence of  $NO$ . Their latitude data suggest little variation at 18.3 km between  $30^\circ$  and  $60^\circ N$  for summer conditions. At 21.3 km an increase of about a factor of two is observed from  $30^\circ$  to  $60^\circ N$ . Their data also suggest a strong seasonal dependence of  $NO$  at both 18.3 and 21.3 km with about an order of magnitude increase from January to July between  $33^\circ$  and  $48^\circ N$ . The higher mixing ratios obtained for the present two northern flights tentatively support an increase in  $NO$  with increasing latitude if a straight comparison at geometric altitudes is made. However, an obvious seasonal effect is not distinguishable from the limited number of balloon flights reported here. Instead, the data suggest that substantial natural variability occurs.

Short-term variability is indicated by differences in the two Churchill profiles which were obtained only 6 days apart, with similar tropopause heights. Shorter-term variability still was observed during the two-hour float period of the November 13, 1973 flight. During the first part of the float period between 0910 and 0950 LT the  $NO$  mixing ratio increased from about 1.7 to 2.8 ppbv. Similar observations of a steady increase of  $NO$  after UV sunrise until about local noon have been made. (Ridley *et al.*, 1975b; Burkhardt *et al.*, 1975) This increase can be interpreted as a result of photolysis of  $N_2O_5$  formed during the night. However, during the subsequent hour of the float period of the flight of Nov. 13 the  $NO$  decreased from 2.8 to about 1.0 ppbv. This short-term decrease does not have a ready photochemical explanation and is therefore most likely a result of natural variability. Substantial variability has also been observed with long-path IR absorption techniques by Ackerman *et al.* (1975). They observed an increase by factors of about 4 and 6 at the highest and lowest comparable altitudes on flights made one year apart from the same location. Short-term variability is also exhibited in the data reported by Loewenstein *et al.* (1974, 1975). Murcay *et al.* (1974), and Lazrus and Gandrud (1974) have also observed considerable variation in  $HNO_3$ , the predominant  $NO_x$  species below about 27 km.

Fig. 4 shows the data of Fig. 3 relative to the altitude above the tropopause.

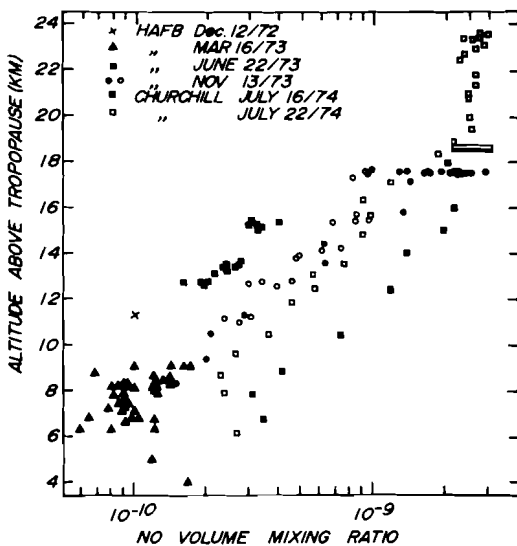


Fig. 4 Same data as Fig. 3 but plotted w.r.t. height above the tropopause.

Over-all, there is some convergence of the Churchill and New Mexico data. The interpretation of such a plot for two different latitudes is not readily made. Since  $O_3$ , temperature, transport and insolation all may change with latitude, the differences are not due to a simple general lowering of the tropopause as northern latitudes are approached. However, the agreement noted may suggest that both latitudinal and seasonal variations should be investigated with respect to the tropopause as well.

Due to the variability of  $NO$ , discussed above, it is difficult to make a detailed comparison of the measurements with models, other than to note that the models appear to represent some mean value of  $NO$ . No present model, either 1-, 2- or 3-dimensional, is able to simulate the variability of  $NO$  noted above.

## 6 Sunset data

In Fig. 5 the measured decay of  $NO$  during sunset is compared with the results of a time-dependent photochemical model. This model includes all reactions and up-dated rate coefficients which have time constants short enough to be of importance in the diurnal variation. The calculation is for the particular date, location and payload altitude of Flight 2. The solid curve of Fig. 5 is the calculated ratio of  $NO_x/NO_{x=90^\circ}$  for the actual temperature and ozone conditions determined for Flight 2. The remaining curves and symbols, as explained in the caption of Fig. 5, illustrate that the computed  $NO_x/NO_{x=90^\circ}$  sunset ratio is fairly insensitive to reasonable ozone and temperature changes. The agreement between the calculated and measured ratio is quite good. For the altitude, temperature and ozone conditions prevailing during the experiment,  $t_1$  is of order a few minutes. Thus, as discussed earlier, the  $NO$  decay is determined primarily by  $t_2$ . A plot of  $t_2$  is shown in Fig. 5. Changing  $O_3$  and/or temperature

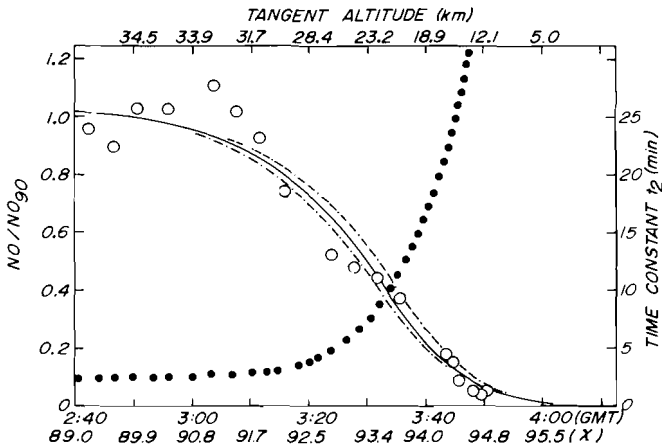


Fig. 5 The sunset decay of nitric oxide versus GMT time and solar zenith angle at the constant float altitude of  $34.5 \pm .5$  km, on Flight 2 (22 July).

*Solid circles:* Time constant  $t_2 = \frac{1}{J_{NO_2+k_2}[O]}$  as calculated from model (a) below.

*Open circles:* The calculated ratio of the measured nitric oxide mixing ratio to the average high sun ( $\chi \lesssim 90^\circ$ ) measured value of 2.7 ppbv.

*Full line:* Model calculation (a) using the measured  $O_3$  temperature data and for the location of the payload at an altitude of 34 km.

*Dash-dot line:* Model calculation (b); same as (a) except that the  $O_3$  concentration was arbitrarily increased by 30%.

*Double-dash dot line:* Model calculation (c); same as (a) except that the temperature was decreased by  $10^\circ$  C.

will change the absolute amount of  $NO$  but not the shape of the  $NO$  profile as the sun sets.

Burkhardt *et al.* (1975) have reported measurements of  $NO$  during sunset at  $33^\circ$ N in May 1974 which show features of  $NO$  disappearance similar to those of the present results. Their measurements, however, are complicated by a rather severe loss ( $\sim 7$  km) of payload altitude during sunset and by the lack of simultaneous  $O_3$  measurements. In spite of this, the same time-dependent model used here can reproduce their results reasonably well if a typical ozone profile is used, a reasonable total  $NO_x$  profile is adopted, and allowance is made for the loss of balloon altitude.

## 7 Summary

The sunset decay of nitric oxide observed experimentally has been shown to be well-accounted for by a straightforward time-dependent photochemical model. The data also confirm the expected absence of  $NO$  during night-time conditions. The observed differences in the two  $NO$  profiles are not as readily explained. However, the variation does introduce a qualification in the interpretation of simultaneous measurements of  $NO_x$  species obtained by a mixture of *in-situ* and remote-sensing techniques. The latter measurements are, of

course, averages over a much larger scale and over atmospheric paths that extend farther and farther from the payload as the sun sets.

### Acknowledgement

It is a pleasure to acknowledge the help given by L.C. Howlett of Utah State University, N. Foulds and his group from SED Systems Ltd., Saskatoon, and the launch and recovery crew from Raven Industries and the Department of Naval Research. We are also grateful to Wayne Evans of the Atmospheric Environment Service and to the operators of the Churchill Meteorological Station for obtaining the ozone profile for Flight 1. Support for Flight 1 was kindly provided by the National Research Council of Canada and for Flight 2 by the Atmospheric Environment Service of Canada.

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