6.1 Introduction:

The present chapter is intended to bring out the variations, as derived from author's own ion composition measurements, of the important minor neutral constituent Nitric Oxide viz. \([\text{NO}]\). The significance of this chapter lies in the fact, that the measurements are made from equatorial latitudes, over the dip equator. Also comparisons are made with \([\text{NO}]\) values derived by the author from ion composition measured by other working groups from the same station.

The neutral Nitric Oxide \([\text{NO}]\), though a minor constituent plays important roles in the ionization balance of D and E-regions. Photoionization of \([\text{NO}]\) due to solar Lyman \(\alpha\) in the D-region has been pointed out as an important source of D-region ionization (Nicolet 1955). The sensitivity of \([\text{NO}]\) to chemical reactions with other major ionized constituents especially with \(\text{O}_2^+\) is equally important. The \([\text{NO}]\) ions resulting from these processes form one of the main positive ion constituents of the E-regions, while in D-region especially in the middle and low latitudes they present themselves as initial ions from which a variety of other positive ion species are formed by a chain of chemical processes. Shirke and Ganguly (1976) have discussed the
possibility of \([\text{NO}]\) coupling the D and F-region ionization while Pradhan and Shirke (1978) had presented a simplified model for the mesospheric \([\text{NO}]\), and explained many D-region features. Determination of the \([\text{NO}]\) profiles is therefore of fundamental importance for an understanding of the lower ionospheric processes.

The most common technique for determining nitric oxide densities in the mesosphere and lower thermosphere is by means of rocket or satellite borne photometers measuring the resonance fluorescence of the gamma bands; (1500Å - 3200Å) (Barth 1964; Meira 1971; Rusch 1973; Tisone 1973; Feldman and Takacs 1974; Tohmatsu and Iwagami 1975); from the measured emission rate profile (with Rayleigh scattering background subtracted), the vertical column density of \([\text{NO}]\) can be calculated by employing the emission rate factor for the corresponding gamma band. Numerical differentiation of the column density finally leads to the \([\text{NO}]\) density profile. \([\text{NO}]\) profiles have also been deduced from ion composition measurements. A comparison between the airglow and ion techniques shows general agreement above 100 km (Golshen and Sechrist, 1975). Danilov et al (1977) have derived \([\text{NO}]\) densities from simultaneously measured ion composition and electron density at 17°N and 48°N latitudes, and studied the variations in the same. They have detected that \([\text{NO}]\) densities decrease from 110 to 130 km by a
factor of 2-3. Also diurnal changes in the E region were found to be in general small, being larger at higher altitudes. The comparison of the mid and low latitude data revealed hardly any variation in $[\text{NO}]$.

A more direct measurement of the $[\text{NO}]$ density, in principle can be achieved by means of mass spectrometers. The mass spectrometric detection of trace constituents, however in most cases is limited by the interfering background gases produced within the mass spectrometer ion source. This difficulty was overcome by Offerman and Trinks (1971) who employed a cryogenically cooled ion source. Such direct measurement of $[\text{NO}]$ by mass spectrometers and UV photometers yield comparable results within experimental errors (Trinks et al 1978).

From studies of ion and nitrogen chemistry of the E-region (Keneshea et al 1970 and Bowhill 1969; Strobel 1971) it was established that $10^{-1026}$ solar flux ionizes the E-region neutral constituents $\text{N}_2$, $\text{O}$ and $\text{O}_2$ and the ionization products undergo a number of ion-neutral reactions whose end products are the terminal ions $\text{O}_2^+$ and $\text{NO}^+$. Conversion of $\text{O}_2^+$ into $\text{NO}^+$ by $\text{NO}$ plays a significant role in establishing the relative concentration of $\text{O}_2^+$ and $\text{NO}^+$ and $[\text{NO}]$ of the order of $10^6$ to $10^8 \text{ cm}^{-3}$ is inferred from insitu E-region ion composition measurements or electron density (Monro and Bowhill 1969, Monro and Smith 1975). Dayglow
observations confirm the order of magnitude of $\left[ \text{NO} \right]$ deduced from E-region ion composition measurements.

The fast reaction of $\text{N} \left( ^2\text{D} \right)$ with $\text{O}_2$ is generally accepted as the major source of NO in the mesosphere and lower thermosphere (Norton and Barth 1970; Strobel 1972). The photoelectron impact dissociation of $\text{N}_2$ is considered as an important source of $\text{N} \left( ^2\text{D} \right)$ (Zipf 1974). The reactions $\text{N}_2^+ + \text{O}$ and $\text{NO}^+ + e$ are also plausible sources of $\text{N} \left( ^2\text{D} \right)$.

In the present study following the method of Danilov (1972, 1977) $\left[ \text{NO} \right]$ densities are derived from major ion composition measurements and simultaneously measured electron density values. Similar analysis has been done by Narcisi et al (1972) during a PCA event and by Sechrist (1967) during a winter anomaly. Swider (1978) has deduced $\left[ \text{NO} \right]$ densities in the 85-110 km region from several day time composition measurements representing various latitudes, seasons and solar conditions. Abdu and Batista (1979) have used Narcisi's data to derive $\left[ \text{NO} \right]$ densities at a southern temperature latitude.

This study by the author differs from those referred above, in the sense, that measurements from one station, during different geophysical conditions, at different times and at the same time on different days are obtained. Comparisons with results obtained using
To ascertain the merits and demerits of different chemical reactions in the E-region, the loss of $O_2^+$ ions by conversion to $NO^+$ ions mainly due to the ion molecule reactions, are considered.

$$O_2^+ + NO \rightarrow NO^+ + O_2 \quad \cdots(6.1)$$

$$O_2^+ + N \rightarrow NO^+ + O \quad \cdots(6.2)$$

$NO^+$ is lost by means of dissociative recombination according to

$$NO^+ + e \rightarrow N + O \quad \cdots(6.3)$$

Therefore at any time the $[NO^+] / [O_2^+]$ is determined by the equation

$$\frac{[NO^+]}{[O_2^+]} = \frac{[X]}{[N_e]} \gamma X_{NO^+} \quad \cdots(6.4)$$

Where $[X]$ denotes the concentration of $[NO]$ or $[N]$ which ever is dominated and $\gamma$ the corresponding reaction coefficient.

If atomic nitrogen is the dominant species, then as the formation of 'N' itself is strongly dependent on ionospheric processes involving charged particles, it has
to have strong (several orders of magnitude) diurnal variations. The other possible parameter \([\text{NO}]\) is known to have only small variations, because neutral particles take part both in formation and in disappearance of \([\text{NO}]\). Also it has been shown by Danilov (1972) that the parameter \(N_e(\text{NO}^+)/[\text{O}_2^+]\) has little variation during day time. This observation indicates that \([\text{NO}]\) plays the role of \([\text{X}]\) and reaction (6.1) controls the behaviour of ion composition in the E-region. This conclusion is also in agreement with Donahue et al. (1970) in which strong increase of the \([\text{NO}^+]/[\text{O}_2^+]\) ratio during an aurora was observed simultaneously with very high concentration of \([\text{NO}]\).

Following the above arguments, with simultaneously measured ion composition and electron density data one could derive the \([\text{NO}]\) values. All the arguments presented above are valid when \(\text{NO}^+\) and \(\text{O}_2^+\) are the only major constituents which is true at least up to 130 km during day and higher above during night. Above this altitude other reactions will become important and this simple technique cannot be used any more. This sets an upper limit to the altitude up to which reliable \([\text{NO}]\) densities could be measured.

6.2 \([\text{NO}]\) densities at the dip equator:

The ion density profiles discussed in chapter III and electron density profiles obtained simultaneously were used in the present analysis. The profiles obtained are
grouped together to study their possible day-night and
day-day variations.

Figure 6.1a (p. 151a) depicts the \([NO]^-\) densities
obtained for the flights from Thumba. Profile labelled 1
corresponds to noon time measurements. During night, the
molecular oxygen density was at the threshold of the
detector sensitivity, suggesting that \(O_2^+\) densities are
not more than 8-10\% of the total. This sets a lower limit
to \([NO]^-\) concentration. \([NO]^-\) estimates show that it is
not less than \(3 \times 10^7\) cm\(^{-3}\) at E-region altitudes at night
and is represented by a straight line (Profile 2). This
suggests a possible day to night variation in \([NO]^-\); the
night-time values being larger than the day time ones.
Profile 3 represents a morning time \([NO]^-\) distribution,
while the night-time representative value at an altitude
nearly 4 hrs before the morning measurement is labelled
as 4. On this occasion \(O_2^+\) densities were extremely low
around 1\% of the total contribution. \(Si^+\) (26\+) were
recorded all through the flight sometimes as large as 10\%
of the ambient density. For an altitude of 105 km where
usually the \([NO]^-\) densities maximise the value obtained
is indeed large and is about \(3.2 \times 10^8\) cm\(^{-3}\).

For the sake of comparison, \([NO]^-\) values derived by
the author from a series of NASA ion composition measurements
from Thumba on an entirely different occasion (Goldberg
et al 1974) are also plotted along with. Profiles
Fig. 6.1: a) Day to night variation in the Nitric Oxide $[\text{NO}]$ as derived from ion composition.

b) $[\text{NO}]$ as obtained from two flights spaced by just two hours.
labelled 5 and 6 in fig. 6.1a correspond to these measurements. Though measurements are available from as low as 85 km because of the problems associated with the hydrated ions normally present in the D-region, only measurements at and above 100 km are considered. Profile 6 corresponds to evening measurements (1938 hrs) and 5 represents the values at midnight on the same day. Once again it is demonstrated that the midnight values are larger than the day time values; sometimes larger by a factor of 4 around 110 km.

In the same context two day time measurements, on the same day, spaced only by two hours are represented by profiles 1 and 2 in fig. 6.1b corresponding to $\chi = 27.8^\circ$ and $\chi = 53.2^\circ$ respectively (Aikin and Goldburg, 1973). For the later flight, data were made available only upto 100 km. But the value at 100 km is nearly 3.5 times larger than the earlier flight. The possible cause of these variations are discussed later.

6.3 Day to day variability:

The day to day variability of $[\text{NO}]$ at the equator as derived from ion composition are presented figure 6.2 (p. 152a). Profiles 1-3 represent the values obtained during sunrise. Profiles 1 and 2 are obtained on consecutive days and 3 was obtained on a different occasion. The day to day variability is really large sometimes
THUMBA

DAY TO DAY VARIABILITY OF NITRIC OXIDE

Fig. 6.2: Day-day variability in [NO] as obtained over Thumba.
variations are by an order of magnitude. Also presented is the direct UV photometer measurements by Tohmatsu and Iwagami (1975) which are the first such direct measurements over the equator, for comparison. The time of measurements also coincides with the other profiles, \( \lambda \) being 82°.

From the author's measurements it was not possible to get the values at the altitude of maximum density. Though from the trend, of the variation of the derived values with altitude it could be said to lie around 105±5 km. The direct photometer measurements and the profile 1 differ by 2 orders around the altitude where \( [\text{NO}] \) maximises. This difference even if attributed to be due to the different techniques of measurement, the differences as obtained in profiles 1, 2, and 3 in figure 6.2 could not be ignored. As the technique is one and the same there could not be any systematic errors. The possible cause for such large day to day variabilities are discussed below.

6.4 Discussion:

The \( [\text{NO}] \) density profiles as derived from ion composition reveal that there seems to be a systematic day to night variation, the night values being larger by a factor of 1.8-2 than the day time values. Also the day to day variabilities are observed to be very large,
and variations as large by a factor of five is not uncommon in the early morning hours. Golshen and Sechrist (1975) in a study of the seasonal and solar cycle variation of E-region nitric oxide, as derived from ion composition have reported a possible increase of \([\text{NO}]\) at 105 km with sunspot number; the increase being by an order of magnitude from quite sun to active sun conditions. As for the seasonal variations are concerned they had concluded that there was a definite trend of increasing \([\text{NO}]\) from winter to summer and had reported ambiguity in \([\text{NO}]\) below 90 km. Golshen and Sechrist (1975) had made use of day time midlatitude E-region ion composition profiles obtained from years 1958-1972. From the author's own analysis it is shown that \([\text{NO}]\) densities could change by a factor of '2' within two hours around 100 km altitude. Also day to night variation by a factor of 2 and large day to day variability by a factor of 5-10 calls for an explanation. Profile 3 in figure 6.2, was obtained during winter and is consistently smaller than 1, and 2, and qualitatively agrees with Golshen and Sechrist's conclusion. The large difference between 1 and 2, obtained on consecutive days is interesting and is discussed below.

The dynamical phenomena in the equatorial ionosphere may possibly be playing a role in the sort of values obtained for \([\text{NO}]\). The author's measurements were either at midnight or at early morning hours except one (Flight No.05.22). The role of dynamics has been brought
out clearly in chapter II as an explanation for the enhanced ionization during night-time around 100 km. In the present context the ratio $\frac{[NO^+]}{[O_2^+]}$ is the one that is used as an indicator of $[NO]$. $NO^+$ is the major ion measured in all the flights and it had been discussed in chapter II, that the transport effects play an important role in the redistribution of this constituent. During night-time when usually the drift direction is downward, $NO^+$ densities increase in the E-region altitude. Therefore one could say that the transport plays the role of an additional source of $NO^+$ apart from chemistry. The neutral densities of $[NO]$ when derived on the basis of chemistry alone are expected to be significantly higher than the actual values. Further the transport parameter is known to vary significantly from day to day (Balsley and Woodman 1969). The life time of $NO^+$ ions being of the order of 3 hours at E-region altitudes, during night, the highly variable transport term could possibly be causing the large day to day variability at the equator. It is recalled that the suggestion of the transport being important has been made also in the discussion of the relative ion density profiles in chapter III.

As for the short period changes during day time, it is not expected to be due to any transport effect. Order of magnitude calculations reveal that the life time of $NO^+$ at E-region altitudes is around 20 sec.
The transport effects are not expected to be very significant within this duration. The maximum ion velocities around 120 km for a primary field of 1 mV/m is around 60 m/sec. (Chapter II, figure 2.8 (p. 70a). At the most, the ions would be lifted up or brought down by a few km before dissociatively recombining with the electrons. As the ion velocity profile shows sharp decrease above and below 120 km the displacements would indeed be very less.

Therefore one arrives at the conclusion that a knowledge of the transport term is a must to explain the possible day-to night variation of $[NO]$. While for day time variations at equatorial latitudes it may not be significant.

It is suggested that more systematic studies including the dynamical parameters be made in order to explain the observed variations more completely.