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NITRIC OXIDE HEIGHT DISTRIBUTION IN THE LOWER IONOSPHERE FROM ROCKET  
ION COMPOSITION RESULTS OVER A SOUTHERN TEMPERATE LATITUDE STATION.

by

M.A. Abdu and Inez S. Batista

Conselho Nacional de Desenvolvimento Científico e Tecnológico - (CNPq)

Instituto de Pesquisas Espaciais - (INPE)

12.200 - São José dos Campos, SP., Brazil

Ion composition results obtained by Narcisi et al. (1972) from rocket observations carried out during the November 1966 solar eclipse campaign at Cassino, south Brazil, are analysed on the basis of the presently known detailed ion chemistry of the lower ionosphere, to deduce the height distribution of nitric oxide concentration in the region from 80 to 110 km. The results are compared with certain available experimental determinations of the NO height distributions carried out by other workers at other places using rocket borne radiometric measurement of NO  $\gamma$ -band emissions in the day glow.

## INTRODUCTION

Nitric oxide plays important roles in the ionization balance of the D and E regions of the ionosphere, through its photo ionization by the solar Lyman  $\alpha$  radiation and its sensitivity to chemical reactions with the other major ionized constituents, especially with  $O_2^+$ . The  $NO^+$  ions resulting from these processes form one of the main positive ion constituents of the E region, while in the D region, especially, of the low and middle latitude ionosphere, they present themselves as the initial ions, from which a variety of other positive ion species are formed by a chain of chemical processes, whose detailed schemes and rate coefficients continue to be one of the major problems of the D region. Determination of the height distribution of the NO concentration is, therefore, of fundamental importance for an understanding of the lower ionospheric processes.

Since the first measurement by Barth (1966) and the later measurement by Meira (1971) of the  $[NO]$  height distribution over middle latitude from rocket observation of fluorescence of the NO  $\gamma$  - bands in the day glow, a few other measurements employing similar technique have been reported for different locations and local times (Witt et al., 1973, Tisone, 1973, Tohmatsu and Iwagami, 1976). On the other hand, the sensitive role of NO in the chemistry of the lower ionosphere ion composition mentioned above, has lead to the deduction of its density also from ionospheric measurements. Estimates of the NO concentration in the D region from

ion composition measurements during a polar cap absorption event (Narcisi et al., 1972) have yielded values intermediate between those of Barth's and Meira's. Sechrist (1974) calculated NO densities from ion composition ( $O_2^+$  and  $NO^+$ ) measurements carried out during a winter anomalous absorption event and obtained values comparable to Meira's results. In this paper, we have deduced the NO height distribution, in the 80 to 106 km height region, using the ion composition results measured by Narcisi et al. (1972) in connection with the 12th November 1966 solar eclipse campaign conducted in Cassino, south Brazil. The deduced NO profile, which probably represents the first determination of its kind over a southern hemisphere location, is compared with some of the experimental determinations of NO profile over other locations.

#### METHOD OF DERIVING THE NO DENSITY

The number densities of  $NO^+$  and  $O_2^+$  and the total ion densities ( $\sum N_i^+$ ) measured during the certification flight by Narcisi et al. (1972) in the 80-106 km height region are used to derive the NO density profile. The main production sources of the  $NO^+$  ions in this height range are (1) the photo ionization of NO by the solar Lyman  $\alpha$  and (2) charge transfer reaction,  $O_2^+ + NO \rightarrow NO^+ + O_2$ ; the  $O_2^+$  itself being produced by the ionization of  $O_2$  and  $O_2(^1\Delta_g)$  by the solar Lyman  $\beta$ , EUV and X-radiations in the 1 - 100  $\overset{0}{\text{A}}$  band. In the lower part of this height region most of the  $NO^+$  and  $O_2^+$  produced are lost through chemical reactions, leading to the

formation of the hydrates of these ions, as the initial processes in the water cluster ion chemistry, before their dissociative recombination with electrons. The latter becomes the important loss process of these ions only above, approximately, 90 km. The  $[NO^+]$ ,  $[O_2^+]$  and  $\sum N_i^+$  measured by the rocket depend, therefore, in a rather complicated way, on the processes involved in the water cluster positive ion chemistry, at the lower heights, and on relatively simple and better understood ionic processes at the higher heights. Our deduction of the NO density makes use of the  $[NO^+] / [O_2^+]$  ratio and the  $\sum N_i^+$  measured by rocket and is briefly as follows.

Using the detailed ion chemistry model for this height region, we derive expressions for the  $[NO^+] / [O_2^+]$  ratio and  $\sum N_i^+$ , which are functions of the  $[NO]$  and the production rates, mainly, of the major initial positive ions,  $q_{NO^+}$  and  $q_{O_2^+}$ . Then, as a first step, we assume approximate values for the ion production rates, and use the expression for the  $[NO^+] / [O_2^+]$  ratio to determine an  $[NO]$  that makes the observed and calculated  $[NO^+] / [O_2^+]$  ratios equal. In a subsequent step, we evaluate the expression for  $\sum N_i^+$  and compare the calculated  $\sum N_i^+$  with the observed value, to determine more accurate ion production rates that are then used to recalculate the NO density of the first step. By iterating between the two steps of calculation we can obtain the  $[NO]$  and the ion production rates that best explain the observed  $[NO^+] / [O_2^+]$  ratio and the total ion densities simultaneously. Further details of the calculation procedure will be clear in the

course of the discussion to follow. For the sake of brevity of discussion, we give below only a brief outline of the ion chemistry scheme used in the calculation.

The part of the ion chemistry reaction scheme, leading to the formation of water cluster ions, starting from the  $O_2^+$  as the initial ion, is reasonably well established from the works of Fehsenfeld and Ferguson (1969), Ferguson (1971), Narcisi (1972) and Swider and Narcisi (1975), upon which we have based our reaction schemes. The reaction path that is more important, in the case of the low and middle latitude D region, however, is believed to be the one starting with  $NO^+$  as the initial ion. We have based this part of our reaction scheme on the recent works of Thomas (1976) and Reid (1977), that consider the three-body reactions of  $NO^+$  to form  $NO^+.CO_2$  and  $NO^+.N_2$ , the collisional dissociation of the latter two ions, and the switching reaction of the weakly bound  $NO^+.N_2$  with  $CO_2$  to form  $NO^+.CO_2$ , as the most important stages in the production of  $NO^+.H_2O$ , from which successive clustering reactions proceed. The role of the hydration processes of  $O_2^+$  and  $NO^+$  in determining the ion composition is, generally, not important above approximately 90 km.

Considering the reactions involving  $O_2^+$  and  $NO^+$  in the general chemical scheme we can derive an expression for the equilibrium  $[NO^+] / [O_2^+]$  ratio. Since the full form of this expression obviously becomes fairly complicated, we give below a shorter representation of it, with the discussion of only the most essential aspects:

$$\frac{[NO^+]}{[O_2^+]} = \left( \frac{Q_{NO^+}}{Q_{O_2^+}} (L - M) + D \right) / (F - G - H) \quad (1)$$

where,

$$Q_{NO^+} = q_{NO^+} + a_1 [N_2^+] + b_1 [N^+] + c_1 [O^+] \quad \text{and}$$

$$Q_{O_2^+} = q_{O_2^+} + a_2 [N_2^+] + b_2 [N^+] + c_2 [O^+]$$

$q_{NO^+}$  is the production rate of  $NO^+$ , from photo ionization of NO by the solar Lyman  $\alpha$  radiation, and  $q_{O_2^+}$  is the production rate of  $O_2^+$  by the solar Lyman  $\beta$ , EUV and X-radiation. The coefficients  $a_1$ ,  $b_1$  and  $c_1$  represent the rates at which  $NO^+$  is produced by chemical reactions per unit densities of  $N_2^+$ ,  $N^+$  and  $O^+$  respectively.  $a_2$ ,  $b_2$  and  $c_2$  are the corresponding rates for  $O_2^+$  production.

$L = 1 + \alpha_2 [e]$ , where 1 is the rate at which the  $O_2^+$  is lost in the three body reactions forming  $O_4^+$  and  $O_2^+ \cdot H_2O$ , and  $\alpha_2$  is the dissociative recombination coefficient of  $O_2^+$ . M is a factor representing the rate of  $O_2^+$  production from the collisional dissociation of the  $O_4^+$ .

D is the loss rate of  $O_2^+$  that results in the formation of  $NO^+$  through several reactions, the most important of which is the charge transfer reaction

$O_2^+ + NO \rightarrow NO^+ + O_2$ .  $F = f + \alpha_1 [e]$ , where f is the loss rate of  $NO^+$  to form  $NO^+ \cdot H_2O$ ,  $NO^+ \cdot CO_2$  and  $NO^+ \cdot N_2$ , the initial steps in the water cluster

ion formation, and  $\alpha_1$  is the dissociative recombination of  $\text{NO}^+$ . G and H are factors arising from the collisional dissociations of cluster ions of  $\text{NO}^+ \cdot \text{CO}_2$  and  $\text{NO}^+ \cdot \text{N}_2$ , that provide an  $\text{NO}^+$  source. A second equation can be written down as follows, to represent the measured total ion density:

$$\begin{aligned} \Sigma N_i^+ = & \frac{Q_{\text{NO}^+} + D [O_2^+]}{F - G - H} + \frac{Q_{O_2^+}}{L - M} + [N_2^+] + [O^+] + [N^+] \\ & + \Sigma^m [ \text{NO}^+ \cdot (\text{H}_2\text{O})_i ] + \Sigma^n [ \text{H}^+ \cdot (\text{H}_2\text{O})_j ] \end{aligned} \quad (2)$$

To solve the equations (1) and (2) we assumed the atmosphere model, for the major and minor constituents and temperature, given by Shimazaki and Laird (1972), for summer noon conditions, except for the  $[\text{NO}]$  that we considered as one of the unknown parameters to be determined.  $[N_2^+]$ ,  $[O_2^+]$  and  $[N^+]$ , which are the minor ionic species for most of these heights, can easily be calculated knowing the corresponding ion production rates (as will be described shortly). The production rates of the major initial ions,  $q_{O_2^+}$  and  $q_{\text{NO}^+}$ , are the unknown parameters, besides  $[\text{NO}]$ , to be determined from equations (1) and (2). As a practical calculation procedure, we divided the ion production rates into three groups: (a)  $q_{\text{NO}^+}$ , (b)  $q_{O_2^+}$  produced by the action of the solar Lyman  $\beta$  and EUV on  $O_2$



and  $O_2$  ( $\Delta_g$ ), respectively, and (c)  $q_{N_2}^+$ ,  $q_{O^+}$ ,  $q_{N^+}$  and a small part of  $q_{O_2^+}$ , all produced by the X-rays in the 1-100 Å wave length region. Swider (1969) has calculated ion production rates due to X-rays from the quiet sun, using an X-ray flux which is nearly equal to that measured by the SOLARD satellite on the day of the rocket measurement, which was a quiet day. We have adopted Swider's results to represent the ion production rates of the group (c). The equations (1) and (2) can now be solved iteratively to obtain the values of  $q_{O_2^+}$ ,  $q_{NO^+}$  and  $[NO]$ , remembering (i) that  $q_{NO^+}$  is a function of  $[NO]$  and (ii) the cluster ion densities are functions of the densities of  $NO^+$  and  $O_2^+$ .

As a first step in the calculation, we assumed an approximate value for the  $q_{O_2^+}$ , and evaluated the  $[NO^+] / [O_2^+]$  ratio using an arbitrary  $[NO]$  and a corresponding  $q_{NO^+}$  calculated for a Lyman  $\alpha$  flux of  $3 \times 10^{11}$  photons  $cm^{-2} sec^{-1}$  (based on the flux used by Metchly et al., 1972). The  $[NO]$  is then varied, each time calculating a corresponding  $q_{NO^+}$ , until the observed and calculated  $[NO^+] / [O_2^+]$  ratios are made equal. The  $[NO]$  obtained in this way is a true representation of the ion density measurements only if the  $q_{O_2^+}$  used in this first step is correct. In the next step the  $q_{O_2^+}$  is determined on the basis of the measured total ion density as follows: Since a tentatively correct  $q_{NO^+}$  was determined in the last step, and since the ion production rates due to X-rays are already known, as explained before, the only remaining ion production rate,  $q_{O_2^+}$ , is now adjusted so that the calculated total

ion density is equal to the observed values. (The densities of each of the hydrated ions and other cluster ions were calculated and added to the densities of the initial ions, to obtain the  $\sum N_i^+$  during each calculation step). The  $q_{O_2^+}$  thus obtained is now introduced in the first calculation and the whole procedure repeated, until we obtain the  $[NO]$ ,  $q_{NO^+}$  and  $q_{O_2^+}$  that best explain the measured  $[NO^+] / [O_2^+]$  ratio and the total ion density simultaneously.

#### RESULTS AND DISCUSSION

The  $[NO]$  height profile deduced from the present analysis is plotted in Figure 1, from 80 to 110 km (the values above 106 km are obtained from extrapolation of the results of Narcisi et al.). For comparison we have plotted in the same Figure, the experimental NO profile of Meira (1971), curve (a), measured over midlatitude when the solar zenith angle was  $63^\circ$  (our results correspond to a solar zenith angle of around  $18^\circ$ ). Meira's  $[NO]$  profile revised using the new  $\gamma$  - band emission rates (Barth, 1975) is also plotted in the same Figure as curve (b). Also shown are the midlatitude sunset result (curve 1) and the tropical morning result (curve 2) of Tohmatsu and Iwagami (1976). Above 95 km our results seem to agree with, though somewhat higher than, Meira's values, whereas below 84 km our values are closer to those of the curve 1 of Tohmatsu and Iwagami, resulting in a steeper gradient in height distribution compared to the experimental results. There is a good agreement, however, in the occurrence of a minimum in the NO density

around 84 km in all the profiles. Below 80 km we have extrapolated our [NO] profile, assuming a constant ratio of mixing of NO with the ambient atmosphere. The NO density at 70 km, that resulted from this extrapolation, is found to be an order of magnitude larger than the values determined by Mitra (1966) for this height, from considerations of solar activity changes in the ionizing radiation fluxes in the various wavelength regions.

In pointing out any meaningful differences in the densities of NO at various heights, by comparing our deduced NO values with the experimental profiles, we should consider also the accuracies involved in the derivations of these profiles. Determination of the experimental profile from the NO luminescence method has large uncertainties at lower heights, due to various factors inherent in the technique of the measurement, as shown in the original profiles of Meira, which indicate error bars of factors of 5-6 at heights below 90 km. It will be useful, and perhaps more meaningful too, (Meira, private communication, 1978), to compare the columnar contents of [NO],  $\eta_{\text{NO}}$ , represented by these various profiles. The  $\eta_{\text{NO}}$  above 80 km, derived using the average emission rate at this height taken from the two profiles of Meira (1971), comes out to be  $1.4 \times 10^{14} \text{ cm}^{-2}$ , with an error bar of 12 percent. The emission rate profile of Tohmatsu and Iwagami (1976) for the midlatitude flight (over Japan), curve 1 in our Figure 1, yields  $\eta_{\text{NO}}$  of about  $10^{14} \text{ cm}^{-2}$ , whereas their results for Thumba (India), curve 2, give a lower value of about  $6.5 \times 10^{13} \text{ cm}^{-2}$ . Compared to these results the value calculated from our

deduced NO profile, assuming diffusive equilibrium for the NO height distribution above 110 km, as Barth's (1966) profile indicates, is around  $2.4 \times 10^{14} \text{ cm}^{-2}$ . These differences in the columnar content of the NO appear to be certainly larger than the uncertainty factors involved in the respective methods. Whether these differences are due to the different observational circumstances, namely, local time, location, epoch etc, can be verified clearly only after a careful examination of these various factors in a larger data sample.

The accuracy of our deduced NO densities would depend upon two factors, the more important of them being that of the ion density values themselves. The uncertainty factors in the rocket ion densities have been pointed by Narcisi et al.(1972). While the values above 90 km are sufficiently accurate having an uncertainty of only 20 percent, those below 80 km could be uncertain by a factor of 2. Thus, our results of  $[\text{NO}]$  below 90 km could be somewhat uncertain due to the ion densities used in deriving them having error bars from 20 to 100 percent. If, however, these uncertainties in the ion densities are, to some extent, cancelled out in considering the  $[\text{NO}^+] / [\text{O}_2^+]$  ratio, then the error in the calculated  $[\text{NO}]$  could be reasonably small. Under this assumption, the error bar resulting from a 100 percent error in the  $[\text{NO}^+]$  and  $[\text{O}_2^+]$  values at 80 km is indicated in Figure 1. The other possible source of error in the deduced  $[\text{NO}]$  could be in the atmosphere model used. This will be discussed shortly.

In deriving the  $[NO]$  profile, we have used the temperature dependent reaction coefficients given by (Reid 1977) for the hydration of  $NO^+$  ion, forming  $NO^+ \cdot H_2O$  directly from  $NO^+$ , and through the intermediate formations of  $NO^+ \cdot N_2$  and  $NO^+ \cdot CO_2$ . The thermal break up of the latter ions to form  $NO^+$  is also highly temperature dependent (Reid, 1977). The  $NO^+$  hydration rate would depend, also, upon the mesospheric water vapor concentration. Thus, it can be seen that for a specified  $[NO^+] / [O_2^+]$  ratio and  $\Sigma N_i^+$ , there could be a wide range of combinations of the temperature and water vapour concentration profiles, that could give rise to the same  $[NO]$  profile. Calculations carried out using the  $H_2O$  and temperature profiles of Shimazaki and Laird (1972), plotted in Figure 2, (curves 1 in the a and b parts of the Figure) showed that the  $[NO^+] / [O_2^+]$  ratio is satisfied for the  $[NO^+]$  and  $[O_2^+]$  values that are different from (actually higher than) the measured values. Two other profiles of temperature and  $H_2O$  are also given in Figure 2 (marked 2). When the lower temperatures (curve 2) are used then the  $H_2O$  profile of Shimazaki and Laird (curve 1) could satisfactorily explain the  $[NO^+] / [O_2^+]$  ratio and the ion densities simultaneously. Alternatively, the temperature curve 1 with a higher  $H_2O$  concentration, given by the curve 2 representing 3 times the concentration of Shimazaki and Laird (1972), could also yield the same  $[NO]$  profile. It appears possible, therefore, that the ion composition data can be used to determine a mesospheric temperature profile if the water vapour concentration profile is known and vice versa (see also Hidalgo, 1977).

The densities of the atmospheric major constituents,  $N_2$  and  $O_2$ , used in the calculation, might be thought to influence the deduced  $[NO]$  values.  $N_2$  plays its role through the three body reactions involving  $NO^+$ , and  $O_2$  is responsible for the absorption of the Lyman  $\alpha$  radiation, thereby determining the flux of this radiation available at each height for calculating the ion production rate,  $q_{NO^+}$ . To check upon this possibility we carried out the calculations using the  $[N_2]$  and  $[O_2]$  height distribution given by the US standard atmosphere, model 1976. The values of  $[N_2]$  and  $[O_2]$  in this model differ from those of Shimazaki and Laird (1972) from factors of approximately 0.7 and 1.1, respectively, at 80 km, to factor of approximately 1.7 and 3.0, respectively, at 110 km. To obtain an  $[NO]$  distribution that explains the observed  $[NO^+] / [O_2^+]$  ratio and the  $\Sigma N_i^+$  simultaneously, we had to use the temperature profile and 3.5 times the  $H_2O$  profile of Shimazaki and Laird (1972). (As mentioned before other combinations of the temperature and water vapour profiles could as well have been used). The  $[NO]$  profile that resulted from this calculation was only slightly different from the one shown in Figure 1; the new values being higher by about 3 percent at 86 km, 8 percent at 100 km and 15 percent, the highest deviation, at 106 km. Below 86 km the difference was less than 3 percent.

#### CONCLUSIONS

We have used the rocket ion composition results obtained by Narcisi et al. (1972) to determine the nitric oxide height distribution

in the height region from 80 to 106 km, over a southern hemisphere temperate latitude station. The method of calculation that utilizes the  $[NO^+] / [O_2^+]$  ratios and the total ion densities measured by the rocket yields, besides the  $[NO]$  height distribution, also the major ion production rates,  $q_{O_2^+}$  and  $q_{NO^+}$  (assuming that the ion production rates used by us for the other species, i.e.  $q_{N_2^+}$ ,  $q_{O^+}$  and  $q_{N^+}$ , are correct). The ion production rate results obtained from this calculation is presented in a separate paper, that deals mainly with the problems of particle ionization source in the south Atlantic geomagnetic anomaly (Abdu et al., 1978). The nitric oxide values obtained appears to be, in general, somewhat higher than Meira's (1971) results at heights above 90 km. At lower heights our values are considerably smaller, producing thus a steeper height gradient in NO density distribution in this height region, compared to the other results; but to some extent this might depend also upon the inaccuracies in the ion density values below 90 km, which could be somewhat large as pointed out by Narcisi et al. (1972). The columnar content of the nitric oxide, represented by our deduced profile, appears to be significantly larger than those represented by equatorial and midlatitude experimental profiles. A minimum in the NO height distribution near 84 km is clearly seen in our results and, in this respect, it agrees very well with the experimental profiles. It seems possible to use the present method of calculation to infer also other atmospheric parameters, such as temperature or water vapour concentrations in the mesosphere. Further studies using ion composition results available for other locations and observing conditions are continuing.

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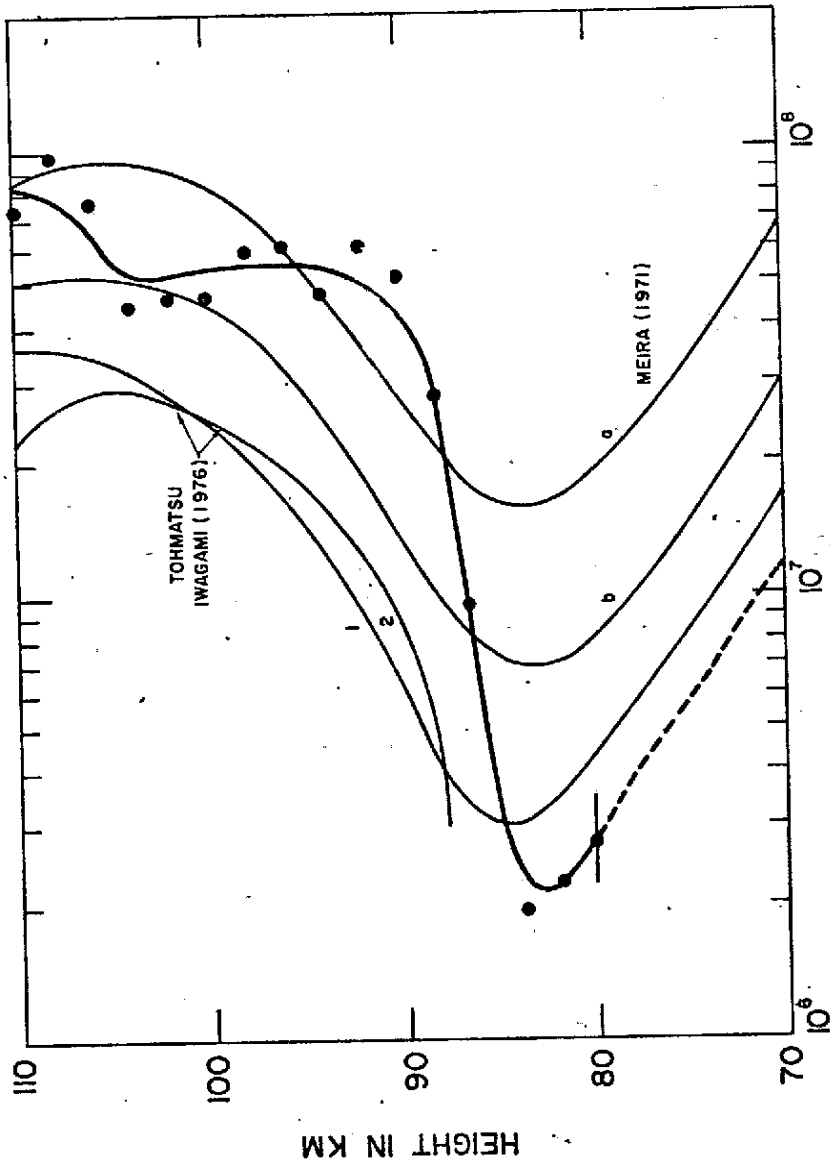
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FIGURE CAPTIONS

Figure 1 - Nitric oxide profile obtained from the present analysis compared to some experimental profiles. Curve (a) is Meira's (1971) original NO profile and curve (b) is profile corrected using the new NO  $\gamma$ - band emission rate. The NO profiles of Tohmatsu and Iwagami (1976) measured under midlatitude sunset condition and tropical morning condition, are shown by curves (1) and (2) respectively. The results of the present analysis are shown by points at intervals of 2 km, through which a smooth profile is drawn.

Figure 2 - The temperature and water vapour profiles used in deriving the [NO] profile from the ion composition results. Curve 1 in the parts (a) and (b) of the Figure are taken from Shimazaki and Laird (1972) - see the text for further details.



NITRIC OXIDE CONCENTRATION (CM<sup>-3</sup>)

Fig. 1 - Nitric oxide profile obtained from the present analysis compared to some experimental profiles. Curve (a) is Meira's (1971) original NO profile and curve (b) is profile corrected using the new NO  $\gamma$ -band emission rate. The NO profiles of Tohmatsu and Iwagami (1976) measured under midlatitude sunset condition and tropical morning condition, are shown by curves (1) and (2) respectively. The results of the present analysis are shown by points at intervals of 2 km, through which a smooth profile is drawn.

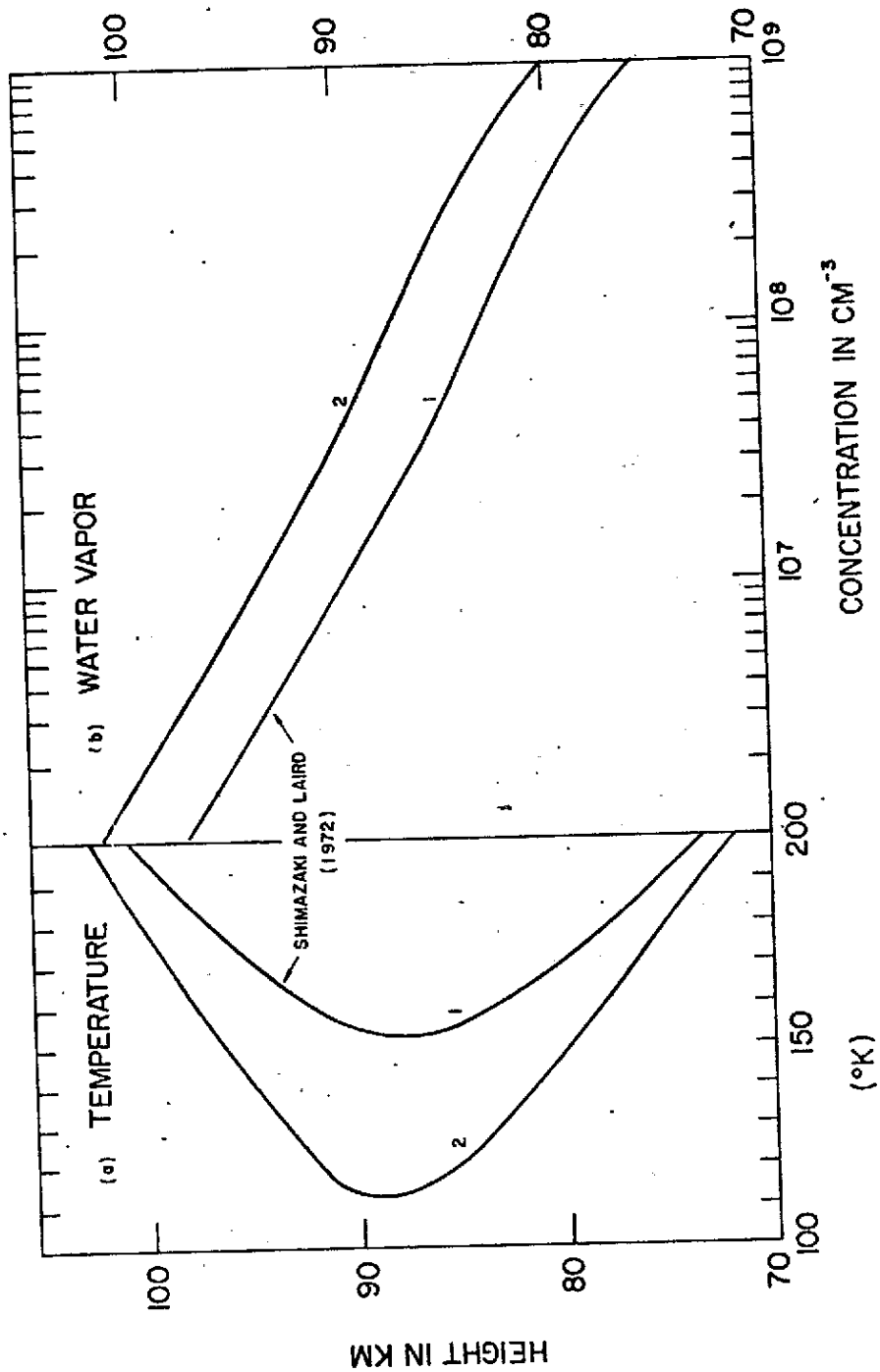


Fig. 2 - The temperature and water vapour profiles used in deriving the [NO] profile from the ion composition results. Curve 1 in the parts (a) and (b) of the Figure are taken from Shimazaki and Laird (1972) - see the text for further details.