

## Mesospheric Nitric-Oxide Concentrations during a PCA

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Atmospheric nitric oxide plays a highly significant role in the formation of the ionospheric *D* and *E* regions. Measurements of its atmospheric concentration and variability are required, therefore, to determine ionospheric behavior. An upper limit to nitric-oxide concentrations was first set by *Jursa et al.* [1959]. Determinations of NO concentrations from rocket-borne ultraviolet spectrometer measurements of the nitric-oxide gamma bands were subsequently reported by *Barth* [1966], *Pearce* [1969], and *Meira* [1971]. Apparently, when Rayleigh scattering is properly subtracted from the emission-rate profiles, the NO-concentration profiles derived by *Barth* and by *Pearce* can be brought more in line with those of *Meira* [1971].

A derivation of daytime, nighttime, and sunset mesospheric nitric-oxide concentrations during a PCA is reported in this paper. These concentrations are calculated by utilizing measured ionospheric parameters and ion-chemical reaction rates exclusively. The PCA measurements are briefly discussed, and it is shown how these measurements were instrumental in clarifying the ion chemistry of the disturbed *D* region. The method of calculation and the measured values of the ionospheric parameters used are discussed. Finally the results are presented and compared to other measurements and determinations.

During the November 2-4, 1969, PCA event at Fort Churchill, Canada, three rocket measurements of the *D*- and *E*-region positive ion composition were performed with cryopumped quadrupole mass spectrometers. Measurements of total charged-particle concentrations were also made with Langmuir probes. The first mass spectrometer was launched on November 3 at 0130 CST ( $\chi = 133^\circ$ ), the second was fired 10 hours later at 1130 CST ( $\chi = 74^\circ$ ), and the third was launched at sunset at 1650 CST ( $\chi = 94.6^\circ$ ) on November 4.

In earlier measurements conducted over Fort Churchill, during more quiescent conditions, water-cluster ions such as  $H^+(H_2O)_n$  were seen to predominate up to 86 km at sunset and at night [*Narcisi*, 1966; *Narcisi and Roth*, 1970]. During the PCA, instead of the expected predominance of water-cluster ions, the positive ion composition was composed almost entirely of  $NO^+$  and  $O_2^+$  in the upper *D* region. Water-cluster ions became predominant below 77 km at night, somewhere below 73 km during the day, and somewhere below 77 km at sunset; the latter two altitudes represent the lowest altitudes where measurements were obtained. The ion-chemical processes known before these measurements led to an immediate emergence of water-cluster ions following ionization by protons, energetic electrons, or X rays. Proton ionization in the *D* region initially produces about 62%  $N_2^+$ , 17%  $O_2^+$ , 14%  $N^+$ , and 7%  $O^+$  [*Swider*, 1969]. Below 90 km, in times of milliseconds these primary ions are converted to about 90%  $O_2^+$  and 10%  $NO^+$  through such well-known reactions as  $N_2^+ + O_2 \rightarrow O_2^+ + N_2$ ,  $N_2^+ + O \rightarrow NO^+ + N$ ,  $N^+ + O_2 \rightarrow O_2^+ + N$ , or  $NO^+ + O$ ,  $O^+ + O_2 \rightarrow O_2^+ + O$ , and  $O^+ + N_2 \rightarrow NO^+ + N$ . The  $O_2^+$  ions were expected to convert immediately to water-cluster ions by the reaction sequence shown in Figure 1 and determined by *Fehsenfeld and Ferguson* [1969] and by *Good et al.* [1970]. Omitting the reaction shown in brackets in Figure 1, and with only 1 ppm of  $H_2O$ ,  $O_2^+$  can be quickly converted to water-cluster ions. The fact that this conversion did not occur during the PCA meant that the clustering chain had to be short circuited in such a manner to regenerate  $O_2^+$ .  $NO^+$  would then become a major ion by  $O_2^+$  charge transfer with NO. These results precipitated further laboratory work and subsequently *Fehsenfeld* [quoted in *Ferguson*, 1971] measured the rate constant for the reaction  $O_4^+ + O \rightarrow O_2^+ + O_3$  to be about  $3 \times 10^{-30} \text{ cm}^3 \text{ sec}^{-1}$ . The reaction  $O_4^+ + O_2(\Delta) \rightarrow O_2^+ + 2 O_2$  may also

## CLUSTERING REACTIONS

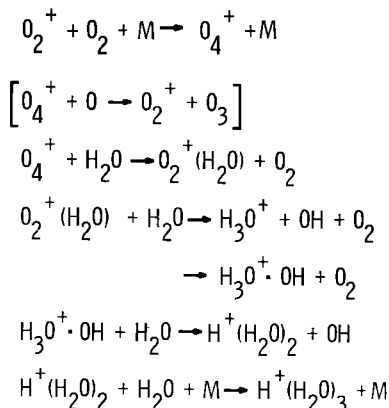


Fig. 1. Reactions that lead to the conversion of  $O_2^+$  to water-cluster ions.  $M$  equals  $O_2$  or  $N_2$ .

be operative, but its rate constant has not been measured. Thus sufficient amounts of atomic oxygen can preclude water-cluster-ion production and regenerate  $O_2^+$  ions in the  $D$  region.

It is interesting to note that the PCA ion-composition measurements seem to reflect the diurnal variation of atomic oxygen. At night atomic oxygen apparently decreases rapidly below 80 km [Shimazaki and Laird, 1970], and water-cluster ions become dominant species below 77 km. In the daytime, when atomic oxygen is enhanced in the  $D$  region, water-cluster ions are not dominant until somewhere below 73 km.

The measured ion composition that is composed mainly of  $NO^+$  and  $O_2^+$  in the range 77–88 km during the PCA can be used to calculate NO concentrations. The calculation is limited to altitudes below 88 km to avoid complexities with metal atomic ions that become important

above 88 km. Only three reactions are considered in the calculation:  $O_2^+ + NO \rightarrow NO^+ + O_2$ ,  $k = 6 \times 10^{-20} \text{ cm}^3 \text{ sec}^{-1}$  [Fehsenfeld *et al.*, 1970];  $O_2^+ + e \rightarrow O + O$ ; and  $NO^+ + e \rightarrow N + O$  with  $\alpha(O_2^+) = 3 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$  and  $\alpha(NO^+) = 6 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$  at  $D$ -region temperatures [Biondi, 1969]. The effects of neglecting the reaction  $O_2^+ + N_2 \rightarrow NO^+ + NO$ , negative ion reactions, and other  $NO^+$  clustering reactions are discussed later. The  $D$ -region electron concentrations during the PCA are typically about  $10^4 \text{ cm}^{-3}$  and larger, and thus equilibrium is established in a matter of a few minutes. The proton flux is assumed constant over this period. Considering only the above reactions, one may write the following two production equal loss equilibrium equations

$$0.9q = \alpha(O_2^+)[O_2^+][e] + k[O_2^+][NO] \quad (1)$$

$$0.1q = \alpha(NO^+)[NO^+][e] - k[O_2^+][NO] \quad (2)$$

where  $q$  is the total proton ion-pair production rate in cubic centimeters per second at a particular altitude and  $[e]$ ,  $[O_2^+]$ ,  $[NO^+]$ , and  $[NO]$  are the various species concentrations in cubic centimeters. As discussed earlier,  $0.9q$  and  $0.1q$  are the  $O_2^+$  and  $NO^+$  production rates, respectively. Solving (1) and (2) for the NO concentration and inserting the rate constants cited yields

$$[NO] = \left\{ 900 \frac{[NO^+]}{[O_2^+]} - 50 \right\} [e] \quad (3)$$

The measured  $[NO^+]/[O_2^+]$  ratios and electron concentrations in 2.5-km increments over the altitude range of interest are given in Table 1. The electron densities were derived from measurements with impedance probes, Langmuir probes, 3-frequency beacons, and ion mass spectrometers [Ulwick, 1971a; Dean, 1970; Narcisi

TABLE 1. Measured  $[NO^+]/[O_2^+]$  Ratios and Electron Concentrations

Altitude, km	$[NO^+]/[O_2^+]$			$[e], \text{cm}^{-3}$		
	Night	Day	Sunset	Night	Day	Sunset
77.5	5.55	1.5		1.2(4)*	2.2(4)	7(3)
80	2.85	0.52	6.8	1.7(4)	3.6(4)	8(3)
82.5	1.45	0.50	5.1	1.9(4)	4.5(4)	9.5(3)
85	1.7	0.45	4.4	1.6(4)	5(4)	1(4)
87.5	2.38	0.72	4.6	1.4(4)	5.7(4)	1.2(4)

\* 1.2(4) =  $1.2 \times 10^4$ .

TABLE 2. Upper Limits for the Rate Constant ( $\text{cm}^3 \text{sec}^{-1}$ ) of  $\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$

Altitude, km	Night	Day	Sunset
77.5	7.7(-17)*	3.7(-17)	
80	8.8(-17)	3(-17)	9.7(-17)
82.5	7.5(-17)	5.7(-17)	1.4(-16)
85	1.2(-16)	8.9(-17)	2(-16)
87.5	2.3(-16)	2.7(-16)	3.8(-16)

\* 7.7(-17) =  $7.7 \times 10^{-17}$ .

*et al.*, 1970]. The accuracy in the derived NO concentrations depends mainly on the errors (in parentheses) in  $k$  ( $\pm 30\%$ ),  $\alpha$  ( $\text{NO}^+$ ) ( $\pm 30\%$ ),  $[\text{NO}^+]/[\text{O}_2^+]$  ( $\pm 30\%$ ), and  $[e]$  ( $\pm 50\%$ ); electron recombination with  $\text{O}_2^+$  has only a small contribution. The  $\text{O}_2^+$  and  $\text{NO}^+$  production rates are believed to be accurate to within  $\pm 0.03 q$ . Therefore the maximum error in this calculation is believed to be  $\pm 140\%$ . However, there may be other sources of error from neglecting other processes, and this possibility is considered next.

It can be shown that omitting the reaction  $\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$  has a generally small effect. An upper limit of its rate constant of  $2 \times 10^{-16} \text{ cm}^3 \text{ sec}^{-1}$  was determined in the laboratory [Shahin, 1967]. In a calculation similar to that for deriving [NO] above but with the assumption now that nitric-oxide concentrations are negligible and that this reaction is the major producer of  $\text{NO}^+$ , upper limits for its rate constant can be calculated by utilizing the ionospheric data in Table 1; these limits are listed in Table 2. A large variability of the rate constant with altitude is seen in Table 2; the calculated values have an associated maximum error of about a factor of 2. If the lowest value in Table 2 of  $3 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$  is taken as the upper limit, the nighttime and sunset nitric-oxide calculations will be essentially unaffected, except at the lowest altitudes where the maximum error at 77.5 km at night is 40%. For the daytime calculations, only the highest altitudes will have a small error. However, the upper limit of  $3 \times 10^{-17} \text{ cm}^3 \text{ sec}^{-1}$  can be lowered significantly if the nitric-oxide concentrations of Meira [1971] are assumed to be present, and thus the omission of this reaction will have a negligible effect in the nighttime and sunset calculations and probably in the daytime calculation as well.

Errors introduced by neglecting ion-ion mu-

tual neutralization processes are also generally small. From the PCA measurements by Ulwick [1971b],  $\lambda$ , the concentration ratio of negative ions to electrons, is unity near 66 km in the daytime and near  $78 \pm 1$  km at night and at sunset. Furthermore,  $\lambda$  becomes rapidly smaller with increasing altitude. The effective mutual neutralization-rate constants were determined by using the measured proton ionization rate and the total positive and negative ion concentrations, and they were found to have values ranging from  $0.5 - 2 \times 10^{-7} \text{ cm}^3 \text{ sec}^{-1}$  below 77 km [Ulwick, 1971b]. Thus for the worst case near 78 km the ion-ion mutual neutralization loss rate for  $\text{NO}^+$  is one-third that of the  $\text{NO}^+$  electron recombination rate. The neglect of negative ion processes then leads to an error of less than 30% near 78 km at night and at sunset, and this error becomes smaller with increasing altitude. In the daytime, the error is entirely negligible. Note that the error due to neglect of mutual neutralization processes tends to increase the NO concentration, whereas the error in neglecting the  $\text{O}_2^+ + \text{N}_2 \rightarrow \text{NO}^+ + \text{NO}$  reaction decreases the NO concentration.

Clustering reactions such as  $\text{NO}^+ + \text{CO}_2 + \text{N}_2 \rightarrow \text{NO}^+ \cdot \text{CO}_2 + \text{N}_2$  with rate constant about  $2.5 \times 10^{-20} \text{ cm}^3 \text{ sec}^{-1}$  at 200°K [Dunkin *et al.*, 1971] also appear to be generally much slower than the  $\text{NO}^+$  electron recombination rate. Between 78 and 88 km, the ion-composition measurements show that greater than 90% of the ions are  $\text{NO}^+$  and  $\text{O}_2^+$ ; therefore, even if such clustering reactions are occurring, the ion composition indicates that these clusters are probably broken up in subsequent reactions so that  $\text{NO}^+$  is reproduced. In summary, the total additional error from these three sources is believed to be less than 30%.

Inserting the values listed in Table 1 into equation 3 gives the results plotted in Figure 2. All of the calculated values lie on the PCA curves shown in Figure 2 with the exception of two points that lie outside the daytime curve but within 20% of the plotted curve. In spite of the large error quoted above, the shapes of the profiles are believed to be significant, because the errors will generally act uniformly to swing the entire profile to higher or lower values. In comparison, Figure 2 shows Meira's [1971] and Barth's [1966] interpretations of their measurements of the NO  $\gamma$  bands. Meira pointed

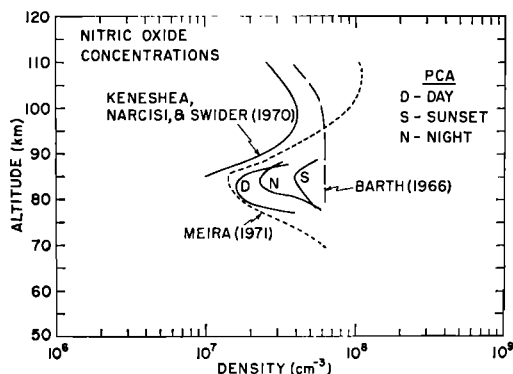


Fig. 2. Nitric-oxide concentrations derived from PCA measurements compared with other measurements and determinations.

out that Barth's values at the lower altitudes shown in Figure 2 can be reduced somewhat when the background due to Rayleigh scattering is properly subtracted. Finally, Figure 2 shows the profile utilized by Keneshea *et al.* [1970] in their diurnal model of the *E* region. Calculations with the Keneshea *et al.* profile exhibit good agreement with midlatitude ion-composition measurements made during the day and night and at about sunrise and sunset. The large errors in all of the profiles shown in Figure 2 of factors of 2 to 3 preclude determinations of temporal changes in NO and possible variations induced by the PCA; only rough upper limits can be inferred. Nevertheless, it now appears that the nitric-oxide concentrations required to describe ionospheric behavior are converging with the directly measured concentrations.

In summary, day, night, and sunset NO concentrations are derived between 77 and 88 km by utilizing rocket measurements of the positive ion composition and charged-particle densities obtained over Fort Churchill, Canada, during the November 2-4, 1969, PCA event. Instead of the expected predominance of water-cluster ions, the positive ion composition between about 77-86 km is composed almost entirely of  $\text{NO}^+$  and  $\text{O}_2^+$  during the PCA. These measurements aided the clarification of the ion chemistry of the disturbed *D* region. The simplified ion composition permits a calculation of NO concentrations from ion-chemical equilibrium relations equating production and loss rates for  $\text{NO}^+$  and  $\text{O}_2^+$ . Through fast chemistry, the ions produced immediately following proton ioniza-

tion are mostly  $\text{O}_2^+$ . The  $\text{NO}^+$  ions are produced principally by charge transfer of  $\text{O}_2^+$  with NO. The derived NO concentrations are within a factor of 2 of  $3 \times 10^7 \text{ cm}^{-3}$  between 77 and 88 km and generally lie between the values obtained by Barth [1966] and by Meira [1971] at mid-latitudes. The three PCA nitric-oxide profiles exhibit minimums near  $84 \pm 1 \text{ km}$ , which are similar to the minimums of the profiles of Meira. There does not appear to be any drastic temporal variation in NO during the PCA.

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