

# Importance of Nitric Oxide in the Atmosphere

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The paper briefly discusses the roles played by nitric oxide, a minor constituent of the atmosphere, in various height ranges, from the troposphere to the lower thermosphere, and comments on some early work of A P Mitra on NO in the mesosphere.

## 1 Introduction

Nitric oxide is a minor constituent of the atmosphere. Its volume mixing ratio in the troposphere is a few parts per billion. The ratio is more at some higher heights, but even in the lower thermosphere, its particle density is several orders lower than that of the major gases. However, it plays major roles in the height ranges from troposphere to the thermosphere, up to the lower F-region of the ionosphere.

In tropospheric chemistry, NO is involved in many reaction chains. In the stratosphere, NO is a major catalytic destructor of ozone. Ionization of NO by solar Lyman- $\alpha$  is a primary source in the formation of the daytime D-region. NO<sup>+</sup> is one of the two major ions (the other one being O<sub>2</sub><sup>+</sup>) in the height range 80-160 km.

NO may be playing important roles in the atmospheres of some other planets as well. Pioneer Venus Orbiter data showed appreciable NO<sup>+</sup> in the ionosphere of that planet<sup>1</sup>.

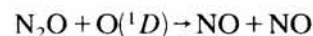
Atmospheric chemistry (both neutral and ion) has been a major area of interest of Dr A P Mitra, and NO in the mesosphere (and later on, the higher oxides, NO<sub>x</sub>, in the mesosphere and the stratosphere) has received his special attention.

This paper attempts to give a brief account of the role of nitric oxide in the aeronomy, from the troposphere to the lower thermosphere. Also, three selected contributions by A.P. Mitra, spanning over three decades, are commented upon, where estimates of NO concentration in the mesosphere (and contributing to D-region ionization) were given, as more and more data became progressively available. A full survey is not attempted.

## 2 Sources of NO

In the troposphere the main source of NO is from fossil fuel burning. Natural sources include lightning discharges and some biogenic production. Indirect

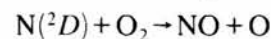
sources are ammonia (NH<sub>3</sub>) from fertilizers and other sources, through a reaction chain and from N<sub>2</sub>O (produced in soils by microbial action and in biomass burning) through photo-dissociation at near-UV wavelengths or through reaction with odd-oxygen



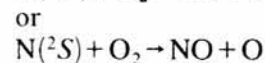
The bulk of N<sub>2</sub>O is transported through diffusion to the stratosphere, where the same processes operate more effectively to produce NO. Downward transport from mesosphere (and thermosphere), solar proton events and high altitude aircraft exhausts are the other sources of NO in the stratosphere.

Main source of mesospheric NO is transport from the thermosphere. Solar proton events and galactic cosmic rays also contribute.

In the thermosphere, NO production is through metastable odd-nitrogen<sup>2</sup>, produced in dissociation of N<sub>2</sub> by XUV photons (800-1000Å) or through photo-electron impact and auroral activity. NO production is through



or



Removal is through



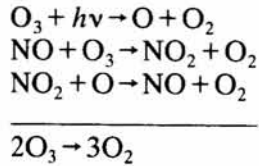
or by downward transport to the mesosphere.

Number densities of NO range from about 10<sup>9</sup>/cm<sup>3</sup> in the stratosphere to 10<sup>5</sup>/cm<sup>3</sup> above 200 km.

NO<sup>+</sup> ions in the mesosphere are produced through photo-ionization by solar Lyman- $\alpha$ . In the thermosphere, however, they are produced in ion-neutral reactions discussed later.

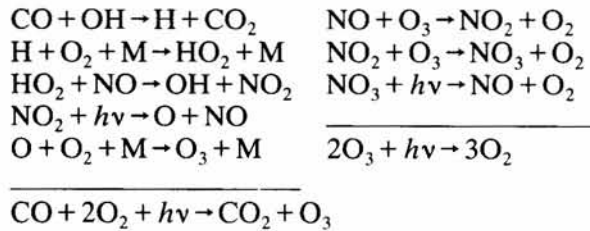
## 3 NO in Troposphere and Stratosphere

The major function of NO is in ozone chemistry. In the stratosphere, it acts as catalytic destructor of ozone through the following reactions:



Other catalytic reactions are also possible.

Catalytic chain reactions in the troposphere, however, lead to increase in  $\text{O}_3$  with increase of  $\text{NO}$  in the troposphere. A possible scheme given by Crutzen<sup>3</sup> is:



$\text{O}_3$  balance is maintained by  $\text{NO}$ , but with increase in  $\text{NO}$ ,  $\text{NO}_3$  may be converted to  $\text{NO}_2$  by a competing process

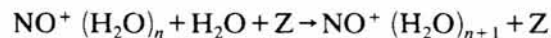


Since  $\text{NO}$  is produced in high temperature combustion, its larger concentration in urban areas contribute to photochemical smog and also to production of higher oxides and  $\text{HNO}_3$ , contributing to acid rain. Sulphur compounds are more effective in this aspect, however.

#### 4 NO in the Mesosphere

The main function of  $\text{NO}$  is in providing ionization to the D-region by solar Lyman- $\alpha$ , which was first surmised by Nicolet<sup>4</sup>. A composite picture of D-region ionization by X-rays, Lyman- $\alpha$  and cosmic rays, in different height ranges, ultimately evolved with Nicolet and Aikin<sup>5</sup>.

Above 82 km, the major ions are  $\text{NO}^+$  and  $\text{O}_2^+$ . At lower heights  $\text{NO}^+$ , produced by Lyman- $\alpha$ , are converted to cluster ions by hydration and three-body reactions, such as



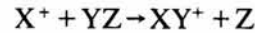
$\text{NO}^-$  is not observed. However,  $\text{NO}$  plays intermediary roles in the formation of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{CO}_3^-$ .

#### 5 NO in the Thermosphere

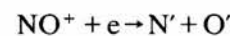
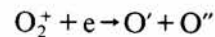
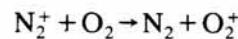
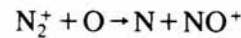
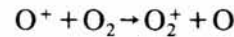
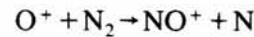
$\text{NO}^+$  is a major ion in the lower thermosphere, but not through direct ionization of  $\text{NO}$ .  $\text{NO}^+$  comes through ion-neutral reactions.

Bates and Massey<sup>6</sup> had described recombination in E- and F- regions in terms of dissociative recombination and conversion of atomic into molecular ions by

charge transfer, and Bates<sup>7</sup> had drawn attention to the need to take into account ion-neutral reactions like



Mass spectrometer measurements, by Johnson *et al.*<sup>8</sup> later, revealed plentiful presence of  $\text{NO}^+$ , even though  $\text{NO}$  was a minor constituent. The relevant reactions are believed to be the following:



$\text{NO}^+$  and  $\text{O}_2^+$  remain the major ions up to about 160 km, above which  $\text{O}^+$  takes over, although  $\text{NO}^+$  in perceptible amount exists even above 200 km.

#### 6 Estimation of NO Concentration in the Mesosphere over the Years

A P Mitra has been active on D-region ionization and  $\text{NO}$  since the 1950s. In an earlier attempt<sup>9</sup>, he formulated an equilibrium distribution model of  $\text{NO}$  in the height range 50-100 km and also considered photo-ionization of  $\text{NO}$  by Lyman- $\alpha$  and an effective recombination co-efficient model involving  $\text{O}$  and  $\text{N}_2\text{O}$ . His estimate of  $\text{NO}$  concentration in 85-95 km range was that it should be less than  $10^{12}/\text{cm}^3$ .

More than a decade later<sup>10</sup>, when D-region electron densities and other data were more reliably available, he utilized electron density profiles deduced by Deeks<sup>11</sup> from VLF observations, for sunspot maximum and minimum years and during equinox, to obtain an  $\text{NO}$  concentration  $\sim 5 \times 10^5/\text{cm}^3$ , around 72 km. This was a remarkable analysis prior to actual rocket measurements of  $\text{NO}$  concentration becoming available.

About another decade later, Mitra and Rowe<sup>12</sup> came out with a detailed analysis considering ground-based and rocket measurements of electron densities, mass spectrometer measurements with rockets, flare and SID observations and attempted reconciling all these aspects. The particle density of  $\text{NO}$  in the mesosphere had, by this time, been identified as between  $10^7$  and  $10^8/\text{cm}^3$ . D-region modellers these days use  $\text{NO}$  values in the above range.

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