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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-α is a primary source in the formation of the daytime D-region. NO^+ is one of the two major ions (the other one being O_2^+) 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^+ in the ionosphere of that planet[1].

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_x, 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_3) from fertilizers and other sources, through a reaction chain and from N_2O (produced in soils by microbial action and in biomass burning) through photo-dissociation at near-UV wavelengths or through reaction with odd-oxygen

$$N_2O + O(^1D) \rightarrow NO + NO$$

The bulk of N_2O 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[2], produced in dissociation of N_2 by XUV photons (800-1000Å) or through photo-electron impact and auroral activity. NO production is through

$$N(^2D) + O_2 \rightarrow NO + O$$

or

$$N(^2S) + O_2 \rightarrow NO + O$$

Removal is through

$$N(^2S) + NO \rightarrow N_2 + O$$

or by downward transport to the mesosphere.

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

NO^+ ions in the mesosphere are produced through photo-ionization by solar Lyman-α. 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:

$$O_3 + h\nu \rightarrow O + O_2$$
$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O \rightarrow NO + O_2$$
$$\overline{2O_3 \rightarrow 3O_2}$$

Other catalytic reactions are also possible.

Catalytic chain reactions in the troposphere, however, lead to increase in O_3 with increase of NO in the troposphere. A possible scheme given by Crutzen[3] is:

$$CO + OH \rightarrow H + CO_2$$
$$H + O_2 + M \rightarrow HO_2 + M$$
$$HO_2 + NO \rightarrow OH + NO_2$$
$$NO_2 + h\nu \rightarrow O + NO$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$\overline{CO + 2O_2 + h\nu \rightarrow CO_2 + O_3}$$

$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
$$NO_3 + h\nu \rightarrow NO + O_2$$
$$\overline{2O_3 + h\nu \rightarrow 3O_2}$$

O_3 balance is maintained by NO, but with increase in NO, NO_3 may be converted to NO_2 by a competing process

$$NO_3 + NO \rightarrow 2NO_2$$

Since 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 HNO_3, contributing to acid rain. Sulphur compounds are more effective in this aspect, however.

4 NO in the Mesosphere

The main function of NO is in providing ionization to the D-region by solar Lyman-α, which was first surmised by Nicolet[4]. A composite picture of D-region ionization by X-rays, Lyman-α and cosmic rays, in different height ranges, ultimately evolved with Nicolet and Aikin[5].

Above 82 km, the major ions are NO^+ and O_2^+. At lower heights NO^+, produced by Lyman-α, are converted to cluster ions by hydration and three-body reactions, such as

$$NO^+ (H_2O)_n + H_2O + Z \rightarrow NO^+ (H_2O)_{n+1} + Z$$

NO^- is not observed. However, NO plays intermediary roles in the formation of NO_2^-, NO_3^-, and CO_3^-.

5 NO in the Thermosphere

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

Bates and Massey[6] 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[7] had drawn attention to the need to take into account ion-neutral reactions like

$$X^+ + YZ \rightarrow XY^+ + Z$$

Mass spectrometer measurements, by Johnson *et al.*[8] later, revealed plentiful presence of NO^+, even though NO was a minor constituent. The relevant reactions are believed to be the following:

$$O^+ + N_2 \rightarrow NO^+ + N$$
$$O^+ + O_2 \rightarrow O_2^+ + O$$
$$N_2^+ + O \rightarrow N + NO^+$$
$$N_2^+ + O_2 \rightarrow N_2 + O_2^+$$
$$O_2^+ + e \rightarrow O' + O''$$
$$NO^+ + e \rightarrow N' + O'$$

NO^+ and O_2^+ remain the major ions up to about 160 km, above which O^+ takes over, although 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 NO since the 1950s. In an earlier attempt[9], he formulated an equilibrium distribution model of NO in the height range 50-100 km and also considered photo-ionization of NO by Lyman-α and an effective recombination co-efficient model involving O and N_2O. His estimate of NO concentration in 85-95 km range was that it should be less than $10^{12}/cm^3$.

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

About another decade later, Mitra and Rowe[12] 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 NO in the mesosphere had, by this time, been identified as between 10^7 and $10^8/cm^3$. D-region modellers these days use NO values in the above range.

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