A Simulation Study of Stratospheric Chemical Reactions Induced by Astronomical Ionizing Events

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Introduction

Chemical kinetic studies of astronomical ionizing events at the stratosphere

Terrestrial consequences of astronomical transient events, such as solar proton events and supernovae, have attracted researchers both in astronomy and aeronomy. Introducing a chemical kinetic approach where radiolysis of gases induced by high-energy protons/photons are explicitly included, we performed a simple calculation as the first step with selected ion-molecule reactions to see the formation of NOx (reactive nitrogen) in the N_2-O_2 atmosphere.

Our Approach

From simple model calculation to large-scale simulations

the present study

BOX MODEL
reations induced by astronomical ionizing events

Analysis of Results
Including new reactions

A new Compilation of Stratospheric Chemical Reactions

Data Analyses

Results as input parameters

Large-Scale Simulation
Chemistry climate model simulation

Solar Proton Events

High-energy protons as the reaction trigger

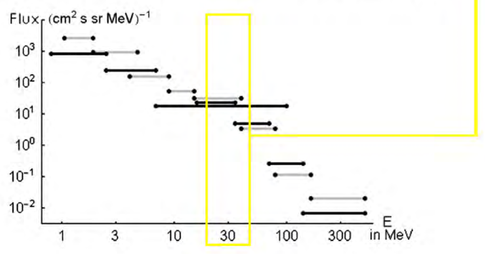
Solar proton events (SPEs) are those where high-energy particles (mostly protons of energies from 10 - 500 MeV) are emitted from the surface of the sun during large solar flares. It is known in the >30 MeV energy range that the most commonly occurring SPEs have an omnidirectional fluence in the 10^5 to 10^6 cm^{-2} range. Very large SPEs exhibit 3 orders of magnitude larger fluence of >1 x 10^9 cm^{-2}. These very large events only occur a few times in a single 11-year solar cycle.

Assumptions for simplified SPE spectrum:

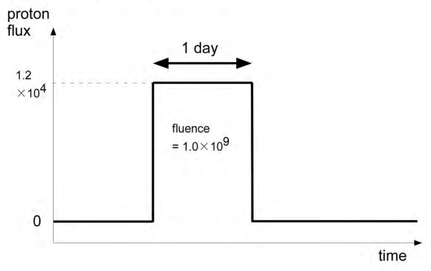
As the 1-st step simulation, we used a step-function following the treatment by Thomas et al. [1].

- Omnidirectional solar proton fluence = 1 x 10^9 cm^{-2} at energies >30 MeV
- Typical duration time = 1 day
- Typical energy of solar protons = 30 MeV

Power spectrum
for the full October / November 2003 event series [2]



Assumed time-profile of the input proton flux



Simulation Method

Starting with the simplest case

Homogeneous Chemical Kinetics (BOX model) with 53 reactions

We used an Integrator (FACSIMILE, mcpa corp.) to solve differential equations.

Assumptions for atmosphere

- Temperature = 223 K
- N_2 density = 7.9× 10^{17} [cm^{-3}]
- O_2 density = 1.7×10^{17} [cm^{-3}]
- No sunlight

Summary

- We performed a simple model simulation of the stratospheric radiolytic and chemical reactions induced by high-energy protons.
- With simplified initial conditions, the reactions in the N_2-O_2 atmosphere were reasonably simulated as the first step.

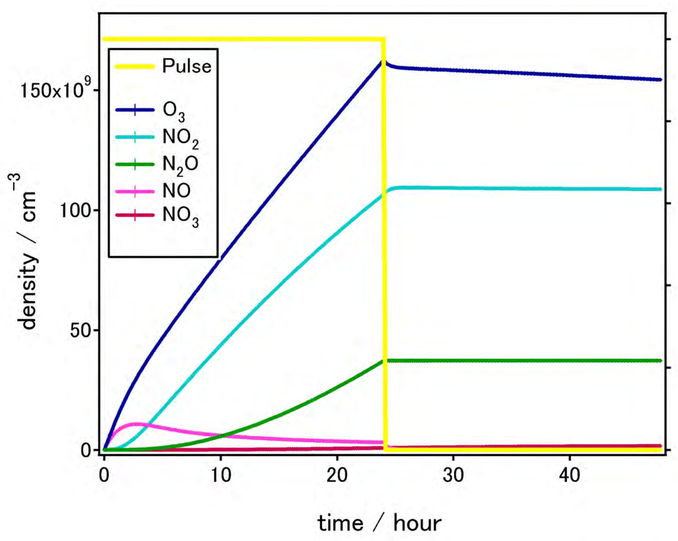
Future Plans

- Realistic input spectra (also for high-energy photons)
- To improve the compilation of ion-molecule reactions
- Advanced (3D Chemistry Climate Model) simulation

Simulation Results

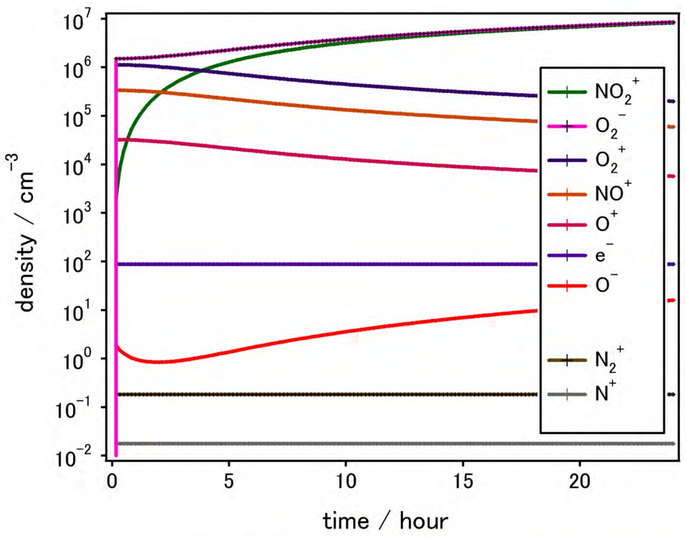
Preliminary results obtained by FACSIMILE

O_3, NO, NO_2, NO_3 and N_2O



In the duration of the energy-input pulse, O_3, NO_2, NO_3,and N_2O increase monotonically and rapidly.

Positive and Negative Ions



Density of N_2^+ and N^+ are extremely small due to the fast reactions. (See the reaction rates shown in the right.)

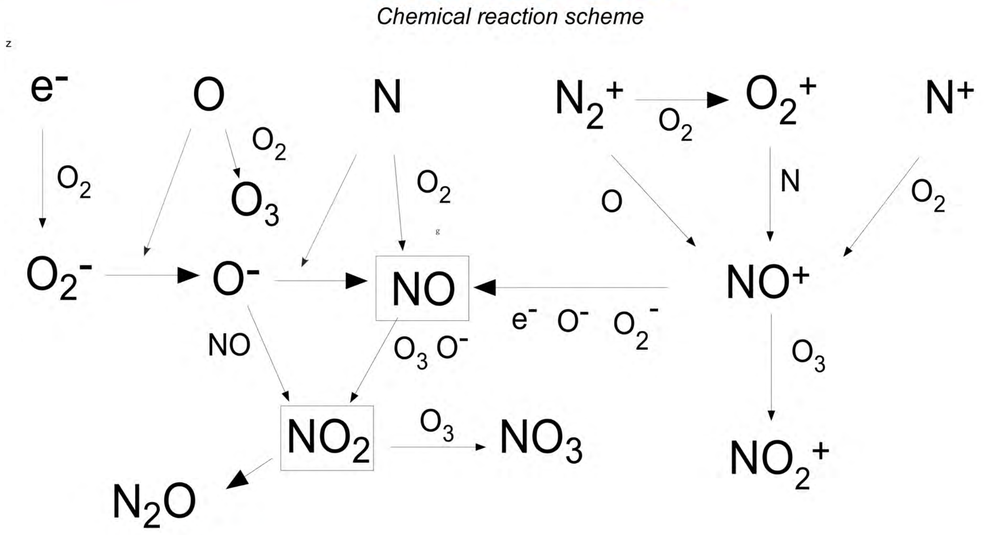
Initial Radiolytic Reactions

Production of ions and radicals from N_2-O_2 atmosphere

Reactions	G Values (atoms / 100 eV)
$N_2 \rightarrow N_2^*$	0.29
$N_2 \rightarrow N_2^+ + e^-$	2.27
$N_2 \rightarrow N^+ + N(^4S) + e^-$	0.69
$N_2 \rightarrow N(^4S)$	1.18
$N_2 \rightarrow N(^2D)$	0.885
$N_2 \rightarrow N(^2P)$	0.295
$O_2 \rightarrow O_2^*$	0.077
$O_2 \rightarrow O(^3P) + O(^1D)$	1.82
$O_2 \rightarrow O(^3P) + O^*$	0.18
$O_2 \rightarrow O(^3P) + O^+ + e^-$	0.80
$O_2 \rightarrow O(^1D) + O^+ + e^-$	0.43
$O_2 \rightarrow O_2^+ + e^-$	2.07

NOx formation

Chemical reaction scheme



Chemical Reactions and Rates

As the first stage of the compilation

Deactivation of $O(^1D)$ and O^*

$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	$k = 5.0 \times 10^{-12}\exp(67/T)$
$O_2^* + O(^3P) \rightarrow O_2 + O^*$	$k = 1.7 \times 10^{-10}$
$O_2^* + O^* \rightarrow O_2 + O(^3P)$	$k = 1.7 \times 10^{-10}$

NO^+ formation through N_2^+, O_2^+, and N^+ ions

$N_2^+ + O_2 \rightarrow O_2^+ + N_2$	$k = 3.9 \times 10^{-10}\exp(-T/143)$
$O_2^+ + N(^4S) \rightarrow NO^+ + O(^3P)$	$k = 1.8 \times 10^{-10}$
$N_2^+ + O(^3P) \rightarrow NO^+ + N(^4S)$	$k = 1.4 \times 10^{-10}$
$N^+ + O_2 \rightarrow NO^+ + O(^3P)$	$k = 2.6 \times 10^{-10}$

NO formation from N, N_2, N^+,O_2^+, O^+, NO^+

$O_2 + N(^4S) \rightarrow NO + O(^3P)$	$k = 4.4 \times 10^{-12}\exp(-3220/T)$
$N(^2P) + O_2 \rightarrow NO + O(^3P)$	$k = 2.0 \times 10^{-12}$

O_2^- formaion

$e^- + O_2 + N_2 \rightarrow O_2^- + N_2$	$k = 3.0 \times 10^{-31}$
$e^- + O_2 + O_2 \rightarrow O_2^- + O_2^+$	$k = 1.2 \times 10^{-29}(300/T)^{1.38} \times \exp(-6602/T)$

O_2^- decrease and O^-, O_3 formation

$O_2^- + O_2^+ \rightarrow e^- + O_2 + O_2$	$k = 2.0 \times 10^{-10}$
$O_2^- + O(^3P) \rightarrow O^- + O_2$	$k = 1.5 \times 10^{-10}$
$O_2^- + O(^3P) \rightarrow e^- + O_3$	$k = 1.5 \times 10^{-10}$

NO^+ decrease

$NO^+ + O_3 \rightarrow NO_2^+ + O_2$	$k = 1.0 \times 10^{-14}$

NO decrease with N

$NO + N(^4S) \rightarrow N_2 + O(^3P)$	$k = 3.25 \times 10^{-11}$

NO_2 decrease

$NO_2 + N(^4S) \rightarrow N_2O + O(^3P)$	$k = 3.0 \times 10^{-12}$
$NO_2 + O_3 \rightarrow NO_3 + O_2$	$k = 1.2 \times 10^{-13}\exp(-2450/T)$
$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$	$k = 2.3 \times 10^{-13}\exp(-1600/T)$
$NO_2 + O(^3P) \rightarrow NO + O_2$	$k = 5.21 \times 10^{-12}\exp(202/T)$

O- decrease

$O^- + N(^4S) \rightarrow NO + e^-$	$k = 2.0 \times 10^{-10}$
$O^- + O(^3P) \rightarrow O_2 + e^-$	$k = 1.9 \times 10^{-10}$
$O^- + NO \rightarrow NO_2 + e^-$	$k = 3.1 \times 10^{-10}\exp(300/T)^{0.83}$
$O^- + O_2^* \rightarrow O_3 + e^-$	$k = 3.0 \times 10^{-10}$

Recombination of O_2^+, O^+, N_2^+, N^+ with electrons

$O_2^+ + e^- \rightarrow O_2$	$k = 4.0 \times 10^{-12}(300/T)^{0.7} + 6.0 \times 10^{-27}(300/T)^{2.5}M$
$O_2^+ + e^- \rightarrow O(^3P) + O(^1D)$	$k = 2.1 \times 10^{-7}(300/T)^{0.55}$
$O_2^+ + O^- \rightarrow O_2 + O(^3P)$	$k = 9.6 \times 10^{-8}(300/T)^{0.5} + 3.0 \times 10^{-25}(300/T)^{2.5}M$
$O_2^+ + O_2^- \rightarrow O_2 + O_2$	$k = 4.2 \times 10^{-7}(300/T)^{0.5} + 3.0 \times 10^{-25}(300/T)^{2.5}M$
$O^+ + e^- \rightarrow O(^3P)$	$k = 4.0 \times 10^{-12}(300/T)^{0.7} + 6.0 \times 10^{-27}(300/T)^{2.5}M$
$O^+ + O^- \rightarrow O(^3P) + O(^3P)$	$k = 2.7 \times 10^{-7}(300/T)^{0.5} + 3.0 \times 10^{-25}(300/T)^{2.5}M$
$O^+ + O_2^- \rightarrow O(^3P) + O_2$	$k = 4.0 \times 10^{-7}(300/T)^{0.5} + 3.0 \times 10^{-25}(300/T)^{2.5}M$
$N_2^+ + e^- \rightarrow N_2$	$k = 4.0 \times 10^{-12}(300/T)^{0.7} + 6.0 \times 10^{-27}(300/T)^{2.5}M$
$N_2^+ + e^- \rightarrow N(^4S) + N(^2D)$	$k = 2.2 \times 10^{-7}(300/T)^{0.39} + 6.0 \times 10^{-27}(300/T)^{2.5}M$
$N^+ + e^- \rightarrow N(^4S)$	$k = 3.5 \times 10^{-12}(300/T)^{0.7} + 6.0 \times 10^{-27}(300/T)^{2.5}M$

Recombination of NO^+

$NO^+ + e^- \rightarrow NO$	$k = 4.0 \times 10^{-12}(300/T)^{0.7} + 6.0 \times 10^{-27}(300/T)^{2.5}M$
$NO^+ + e^- \rightarrow O(^3P) + N(^2D)$	$k = 4.3 \times 10^{-7}(300/T)^{0.8}$
$NO^+ + O^- \rightarrow O(^3P) + NO$	$k = 4.9 \times 10^{-7}(300/T)^{0.5} + 3.0 \times 10^{-25}(300/T)^{2.5}M$
$NO^+ + O_2^- \rightarrow NO + O_2$	$k = 4.0 \times 10^{-7}(300/T)^{0.5} + 3.0 \times 10^{-25}(300/T)^{2.5}M$

O_3 formation through $O(^3P)$

$O + O_2 + M \rightarrow O_3 + M$	$k_0 = 6.0 \times 10^{-34}(300/T)^{2.3}$ $k_\infty = 2.8 \times 10^{-12}$

O_3 decrease

$O_3 + O(^3P) \rightarrow O_2 + O_2$	$k_0 = 8.0 \times 10^{-12}\exp(-2060/T)$
$O_3 + NO \rightarrow NO_2 + O_2$	$k_0 = 1.8 \times 10^{-12}\exp(-1370/T)$

[1] Thomas et al. Geophysical Research Letters 34, (2007) L06810
[2] Bornebusch et al. Advances in Space Research 45, (2010) 632