The response of middle atmospheric ozone to solar proton events in a changing geomagnetic field

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Abstract

This work presents investigations of possible impacts of geomagnetic field variations on middle atmospheric ozone responses to solar proton events (SPEs) by the means of atmospheric modelling.

During SPEs the flux of highly energetic protons from the Sun is markedly increased. In the vicinity of the Earth, strength and structure of the geomagnetic field control the deflection of these particles. At present, the terrestrial magnetic field is dominated by its dipole component, and therefore charged particles from solar eruptions are only able to penetrate into the atmosphere at high latitudes. There the precipitating particles cause perturbations of the atmospheric ion and neutral chemistry, and lead to the formation of reactive NO$_x$ (= N, NO, NO$_2$), and HO$_x$ (= H, OH, HO$_2$) which in turn destroy ozone in catalytic cycles. On geological timescales, the Earth’s magnetic field is subject to significant variations which alter the regions in which charged particles can enter the atmosphere.

In order to study the SPE caused ozone destructions, a two-dimensional atmospheric chemistry and transport model has been used. For the purpose of a proper simulation of the SPE impacts, the existing model has been enhanced by modifications of the mesospheric chemistry scheme, and by the development of an ion chemistry model. The initial disturbances by the precipitating particles have been described by atmospheric ionisation rates which were applied to the atmosphere under the consideration of different shielding properties of the geomagnetic field. The present-day magnetic field configuration and five other scenarios have been analysed. Some of these scenarios are representations of magnetic field reversal situations. Several historical single SPEs have been investigated, and additionally a simulated 200 year time series of SPEs has been used to study impacts on longer time scales.

The simulations have shown that geomagnetic field variations can considerably affect the ozone destructions caused by solar proton events. In all magnetic shielding scenarios the ozone destructions on longer time scales are most pronounced in the polar regions which indicates the importance of the global transport of NO$_x$ and its subsidence into the polar ozone layer. The ozone losses are found to increase with the size of the magnetic cusp and with its nearness to the polar regions. The main reason for this are the atmospheric transport patterns in combination with the stronger photochemical destruction of NO$_x$ at lower latitudes. In comparison with ozone holes, the SPE impacts on polar ozone are less restricted to spring times and early summer. For some of the magnetic field configurations, very large events are able to cause dramatic ozone losses especially in the polar regions and at mid-latitudes, lasting for several months up to years. Basic parametrisations as well as radiative transfer simulations have been used to estimate the corresponding increase of harmful ultraviolet radiation at ground level. Additionally, the temperature changes due to the SPE caused perturbations of the atmosphere’s chemistry have been briefly investigated.
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*Kurt Vonnegut, jr.*

_Cat’s Cradle_
1. Introduction

Ozone is one of the most important atmospheric trace gases. It is an effective absorber of ultraviolet radiation and therefore crucial for protecting any non-aquatic life on Earth against harmful shortwave solar radiation. Additionally, due to its absorption and emission properties, ozone is important for the energy budget and dynamics of the atmosphere. The vulnerability of the atmospheric ozone layer became clear through the discovery of the pronounced ozone losses in the southern polar regions \cite{Farman1985}, commonly known as the Antarctic ozone hole. Since then, the physical and chemical processes which determine the ozone content in the atmosphere have been subject of extensive scientific research. Today the ozone hole phenomenon is believed to be quite well understood, and to be caused by anthropogenic halogen substances \cite{Solomon1999, references therein}.

Ozone is also subject to several natural variations on both local and global scales. For instance, substances released by volcanic eruptions can cause ozone perturbations. Varying atmospheric temperatures, eddy heat fluxes, and atmospheric circulation, which can be caused by either natural or anthropogenic factors, are able to influence the ozone budget as well. There are also extraterrestrial factors that can have impacts on ozone. The solar ultraviolet flux reaching the planet’s atmosphere varies with the solar activity, e.g. the Schwabe (11 year) cycle, and the distance between Earth and Sun. The changing ultraviolet fluxes give rise to varying ozone production and loss rates.

Another reason for ozone perturbations are energetic charged particles of solar and cosmic origin. An important source of such particles in the solar system is the Sun itself. During irregularly occurring so called solar proton events (SPEs), the flux of energetic protons is significantly increased. After these particles have entered the atmosphere they lose kinetic energy through collisional interactions with air molecules and atoms, and produce a number of partly ionised atomic and molecular fragments. Subsequent rapid reactions and recombinations lead to the formation of reactive NO$_x$ ($= \text{N, NO, NO}_2$), and HO$_x$ ($= \text{H, OH, HO}_2$). Both NO$_x$ and HO$_x$ are well known for their ability to destroy ozone in catalytic cycles. Since the pioneering works of Swider and Keneshea \cite{1973}, and Crutzen et al. \cite{1975}, the atmospheric impacts of precipitating energetic charged particles have been investigated in various studies. It is now well established that SPEs can cause considerable atmospheric perturbations and ozone losses in regions where the charged particles enter the atmosphere, but their impacts in terms of total ozone are generally smaller than the typical ozone hole depletions.

The regions in which extraterrestrial charged particles actually can penetrate the atmosphere are determined by their deflection and guidance by the geomagnetic field. Thus, they depend on both the particle’s energy as well as on the structure of the Earth’s magnetic field. Due to its dipole-topography, the present geomagnetic field allows protons in the SPEs’ energy range to enter the Earth’s atmosphere only in the (magnetic) polar regions. Therefore significant SPE caused ozone losses are nowadays restricted to high latitudes.
The terrestrial magnetic field is not static. It is known that during the last centuries the magnitude of the Earth’s magnetic dipole term has significantly decreased. On longer time scales even more pronounced changes of both the geomagnetic field strength and its topology occur. Extreme cases are polarity reversals during which the dipole strength can be drastically reduced, and the field is no longer dominated by its dipole component for several thousand years. From this the interesting question arises how geomagnetic field variations may affect the atmosphere’s protection against energetic solar particles, the particle induced ozone perturbations, and the subsequent effects on ultraviolet absorption. This issue is being addressed in the following.

1.1 Outline of the thesis

This work presents an approach to study the possible impacts of solar proton events on atmospheric ozone for different geomagnetic field scenarios by the means of atmospheric modelling. In order to regard realistic scenarios it is necessary to consider the nature of the Earth’s magnetic field specifically. The consequences of large scale variations in the Earth’s magnetosphere on its shielding efficiency against charged particles from space have been investigated by Vogt et al. [2007]. Motivated by that study, several characteristic field scenarios have been chosen to be analysed with respect to impacts on the atmosphere. The focus lies on field configurations which represent possible situations during field reversals. These field scenarios have been studied in combination with several historical solar proton events. Additionally, in order to investigate impacts of SPEs on the middle atmospheric ozone on longer time scales, a simulated time series of SPEs which covers 200 years has been utilised. For the purpose of these investigations, a two dimensional atmospheric transport and chemistry model has been used. The initial impacts of solar proton events are considered by ion pair production rates which are applied to the model atmosphere. An important part of this study was the enhancement of the existing chemical simulation tools, outlined in section 4, and the development of an ion chemistry model described in section 6. A comparison of simulation results for a single SPE with satellite observations is given at the beginning of section 8.1. Afterwards, the hypothetical geomagnetic field configurations and their atmospheric impacts are approached for single SPEs, and for the long time series in section 8, and section 9, respectively.
2. Some basics

In this section some of the basic principles regarding the Earth’s atmosphere, the Sun and its changing activity, solar proton events and their atmospheric impacts, the geomagnetic field and its variations are outlined. Of course, not all aspects in this wide field can be covered in a few pages and the intention here is to provide a framework that will enable the following sections to be understood. More detailed analysis of these foundations can be sought in the references given in the text. The starting point is the Sun’s atmosphere from where the released energetic charged particles will be traced to the Earth’s atmosphere.

2.1 Solar proton events

On September 1st, 1859, Richard C. Carrington observed a bright outburst at the Sun’s surface while undertaking his customary observation of sunspots [Carrington, 1860]. This event is often referred to as the Carrington white light flare, however it was independently reported on by Hodgson [1860]. Since then numerous solar flares and coronal mass ejections (CMEs) have been detected by the means of ever improving solar observation techniques, and by exploiting proxy data such as nitrate deposit in ice cores [McCracken et al., 2001a], and cosmogenic isotopes in tree rings and ice cores [Solanki et al., 2004, and references therein].

Both solar flares and CMEs are sources of energetic charged particles leaving the Sun’s atmosphere. The ejected plasma fluxes consist mainly of protons, with a variable admixture of He$^{2+}$ and heavier nuclei, and associated energetic electrons. The protons and other nuclei have kinetic energies between several tens of keV and many hundred MeV [Reid, 1986]. As the energetic protons are believed to cause the strongest effects, these plasma ejections are often simply called solar proton events (SPEs).

Almost all of the Sun’s surface phenomena are influenced or even dominated by the magnetic fields of the Sun [Briand, 2003, Sobotka 2003], and solar flares and CMEs are very striking manifestations of the Sun’s magnetic activity. The details of their formations, and the relations between flares and CMEs are still a subject of research, but it seems clear that the huge amounts of energy which accelerate the plasma material and discharge it from the Sun’s surface originate from reconfigurations of the solar magnetic field, see e.g. Emslie et al. [2004]. Another apparent, and related, indication of solar magnetic fields are sunspots, dark surface areas located in regions of strong magnetic flux tubes rising up from the convective zone. Their magnetic nature was revealed in the 20th century by spectroscopic methods (Hale and Nicholson [1938]).

An early dynamic description of the solar dynamo and the formation of sunspots was presented

---

1 The term solar proton event is sometimes instead used for the impacts of the energetic protons in the Earth’s atmosphere (synonymous for PCA - polar cap absorption), and the ejections from the Sun’s surface are then called solar energetic proton/particle (SEP) events.
by Parker [1955]. An overview of the present understanding of the solar dynamo is given by Ossendrijver [2006].

Schwabe [1844] had discovered that the appearance of sunspots is not random but varies with a mean period of about 11 years. The cycle length lies between 9.5 and 12.5 years. The definition has it that a Schwabe cycle begins with a minimum sunspot number (simply called a solar minimum). With an increasing sunspot number the probability for magnetic field line merging rises and therefore more SPEs occur during a solar maximum (figure 2.1). To be more precise: The SPE occurrence probability is related to vanishing sunspots and therefore highest at the trailing edges of the solar activity cycle.

During a cycle period not only the sunspot number changes but also the frequency of sunspot appearances in different regions on the Sun’s surface. This is due to the fact that sunspots occur in regions of concentrated field lines which move towards the equator along a solar cycle (every second solar cycle the Sun’s magnetic field undergoes a polarity reversal). Maunder [1904] illustrated the varying sunspot occurrence in his “butterfly” diagram. Such a diagram is shown in figure 2.2 for the last 12 Schwabe cycles.

The extremely few sunspots present in the second half of the 17th century, are called the Maunder minimum (figure 2.3). Other pronounced minima are believed to have occurred in the past millennia [Stuiver and Braziunas, 1993]. But there are some issues regarding the existence of the Maunder minimum, e.g. Gleissberg [1968]. There is another moderate modulation of the Sun’s activity, namely the Gleissberg cycle which had a minimum around 1825 [Gleissberg, 1944]. The minima of this cycle seem to recur every 80 to 100 years, yet no minimum has been identified in recent times although it is overdue. Reedy [2002] has concluded that it appears as if the Gleissberg cycle had ended, but Landscheidt [1986] had pointed out that the Gleissberg cycle...
length can reach 120 years, complicating the prediction of solar activity. The irregular but
quasi-periodic patterns of solar activity have been related to chaotic processes in the convection
zone. In doing so, the Maunder minimum can be interpreted as spontaneous transitions of fully
turbulent to laminar plasma flows (see e.g. Spiegel, [1987]). There are different approaches
to describe the changing solar activity, including complex nonlinear analyses (e.g. Serre and
Nesme-Ribes [2000]).

2.2 Towards Earth’s atmosphere

As outlined in the previous section, SPEs are results of the Sun’s magnetic activity, and mag-
netic fields also determine the further paths of the ejected charged particles. They experience
forces from the magnetic fields, and gyrate around the field lines while moving away from the
Sun. Due to the different kinetic energies of the particles, the SPE plasma pulse is elongated
on its way. The particles from one ejection typically arrive at the Earth within a time span
of several hours. The large scale magnetic field structures in the solar system are dominated
by the Sun’s field, but in the vicinity of planetary dynamos the field structures are markedly
altered. The Earth’s magnetic field is quite extensive and at present dominated by its dipole
component. The origin of the geomagnetic field and its variations will be addressed in chap-
ter 2.3, but firstly the present magnetic configuration with its effects on energetic charged solar
particles is briefly considered: In isolation, the Earth’s dipolar field would symmetrically ex-
tend to infinity, however its shape is actually distorted by the solar wind, a stream of lower
energetic charged solar particles. As a result, the terrestrial magnetic field is confined to a
finite volume, the magnetosphere. Field lines in the direction of the Sun are compressed, while those at the Earth’s night side are stretched to form the distant magnetotail, which lies well beyond the Moon’s orbital distance from Earth. The solar wind particles generate a standing shock wave around the magnetosphere. The boundary between the surrounding wind plasma and the magnetospheric plasma is called magnetopause. The bulk of the solar wind particles is deflected around the magnetopause without any further interaction with the Earth system. Only at higher geomagnetic latitudes are plasma particles able to penetrate into the magnetosphere via the polar cusps. Here the field strength is extremely low, and the terrestrial magnetic field lines can be merged with the interplanetary magnetic field (IMF). Such configurations are called “open field lines” (figure 2.4) which constitute funnels for the charged solar particles. The process of particle guidance and penetration into the atmosphere is quite complex. The extent to which the particles actually enter the polar cusps depends on their gyro radii and thus on field strength, kinetic energy, and mass-to-charge ratio. Complex calculations are required to assess the energy dependent entering regions for a given field configuration, including particle trajectory tracings in a magnetospheric potential field model [Stadelmann, 2004], or large scale magneto-hydrodynamic (MHD) simulations [Zieger et al., 2006]. The magnetic cusp structures themselves are not static, but depend on a variety of factors. Magnetic field orientations are important for the connection of Earth’s field lines with the IMF. In particular, it is the southward direction of the IMF which controls the structure of the magnetic cusps, see e.g. Fuselier et al. [2002]. Solar wind variations have an influence on the cusps sizes on time scales from hours up to years, and important are the impacts of magnetic storms associated to SPEs. Carrington, as early as 1859, had noticed that the flare of the September of that year was followed by a large magnetic disturbance at the Earth about 17 hours and 40 min later. He hesitated to relate this to the SPE (“one swallow does not make a summer”, [Carrington, 1860]), but later it was shown (Hale [1931], Chapman and Bartels [1940]) that SPEs and magnetic storms are indeed linked. The cusps are enlarged if a SPE related magnetic storm hits the magnetosphere. In such a case the storm reaches the Earth after the most energetic protons have already arrived, giving rise to varying cusp sizes along one SPE pulse. Furthermore, the magnetosphere can be disturbed by storms of previous solar events. Another issue for particle precipitation is that charged solar particles do not only directly enter the atmosphere through the polar cusps but can also be trapped in the Van Allen belts within the magnetosphere. There they mix with particles evaporated from the Earth’s ionosphere, and can later be released to the atmosphere, see for instance Bone [1991].

Figure 2.3: Almost 400 years of observed sunspot numbers. The plotted data are from Hoyt and Schatten [1998] continued with values for recent years from Royet II [2007]. Negative values indicate gaps in the time series.
2.3. The geomagnetic field, and its variations

While the small scale structures of the terrestrial magnetic field are complex, e.g. Campbell [2003], the larger scale basic topology can be described by the field’s first multipole coefficients quite well. Today the geomagnetic field is dominated by its dipole component, tilted by about 11° with respect to the geographical axis. According to Fraser-Smith [1987], the magnitude of the dipole term has decreased within the last 400 years by about 40%. More recently, Gubbins et al., [2006] have stated that the field’s decay before 1840 could have been weaker than previously assumed, but there is agreement on the last century’s slope. On longer time scales even more pronounced changes of both the geomagnetic field strength and its topology occur, see for instance McElhinny and Senanayake [1982]. The terrestrial magnetic field has changed its polarity many times at irregular intervals of about 250 thousand years throughout the geological history. During such a field reversal, the dipole component is depressed to lower than 25% of the present value for several thousand years, and then the field is no longer dominated by its dipole component [Merrill and McFadden, 1999]. Details about geomagnetic field variations can be derived from the worldwide analysis of paleomagnetic proxy data (e.g. Mankinen and Dalrymple, [1979]). The last full polarity reversal, the Matuyama/Brunhes transition, occurred about 780 thousand years ago [Baski et al., 1992]. It is clearly recorded in volcanic and marine material from which the global magnetic field can be reconstructed, e.g. Guyodo and Valet [1999].

A complementary approach to investigate reversals is the analysis of the mechanisms of field generation in the Earth’s core. The understanding of the geodynamo has benefited from detailed numerical simulations (e.g. Glatzmaier et al. [1995], Wicht and Olson [2004]). The most widely accepted theory for the generation of the terrestrial magnetic field is that the Earth’s liquid outer core maintains a self-sustaining dynamo which is driven by the interplay of convections
and the forces of inertia in the rotating frame of reference (e.g. Dormy et al. [2000], Campbell [2003]). Both reconstructions from paleomagnetic proxy data and modelling of the geodynamo indicate that the field’s structure during reversals has significant non-dipolar contributions. More polarity transitions are expected during periods of weak field intensity [Valet et al., 2005], and in simulated reversals the dipole moment drastically decreases, e.g. Glatzmaier et al. [1995]. Under such conditions, the terrestrial magnetic field is strongly influenced by its quadrupole component for several thousand years. Another possible, though less likely, reversal scenario is that the dipole moment still dominates the field, and the dipole axis slowly turns around, staying close to the equatorial plane for a significant time before moving ahead.

The Earth’s varying internal fields affect the structure of the magnetosphere, and thus the regions in which extraterrestrial particles can approach the atmosphere are changed as well. As long as the dipole component dominates, and the dipolar axis is basically parallel to the geographical rotation axis, the principle structure of the magnetosphere remains similar to the present-day situation. The weaker the dipole moment gets, the larger the magnetic cusp regions become [Sisco and Chen, 1975]. Other field configurations give rise to fundamentally different magnetospheric structures. This will be addressed in a little more detail in section 6.4 where the magnetic field scenarios for the simulations are described.

2.4 The Earth’s Atmosphere

2.4.1 Basic description of composition, structure and dynamics

The main constituents of the atmosphere are N\textsubscript{2} and O\textsubscript{2}. Together with the noble gas argon they account for more that 99.9\% of the total mass of the dry atmosphere. All other species are trace gases. Despite their insignificance in percentage terms, some of them are crucial for the radiative transfer and the energetics of the atmosphere. The role of ozone and some other species will be addressed in the next section. Within the homosphere, extending up to a height of about 100 km, fluid motions tend to mix all the gaseous constituents, and only substances with significant sources or sinks have varying mixing ratios. In the homosphere, the thermodynamic quantities pressure \( p \), temperature \( T \), and density \( \rho \) are to a good approximation related by the ideal gas law and the hydrostatic equation,

\[
p = \rho RT \quad \frac{\partial p}{\partial z} = -\rho g
g E.1\]

where \( R \) and \( g \) denote the gas constant of dry air and the gravity acceleration respectively, and \( z \) is the geometric height. This implies that the pressure basically decreases in an exponential manner with height:

\[
p(z) = p_0 \cdot \exp \left[ -\int_0^z \frac{1}{H(z')} dz' \right]
\]

This is the barometric height formula, with \( H = RT/Mg \approx 7 \) km being the atmospheric scale height, that is the height an isobaric atmosphere with pressure \( p_0 \) would have. \( M \) is the mean molecular mass which is nearly constant in the homosphere. At higher altitudes, beyond the homopause, the different constituents separate from each other due to molecular diffusion, and lighter elements dominate at higher altitudes. The so called geocorona finally consists almost entirely of hydrogen. A collection of some atmospheric vertical labels is given in figure 2.5.
A useful quantity for the description of atmospheric processes is the potential temperature

\[ \theta = T \cdot \left( \frac{p_0}{p} \right)^\kappa \]

where \( p_0 \) is a reference pressure at a certain height, e.g. at the Earth’s surface, and \( \kappa = R/c_p \) with \( c_p \) being the specific heat at constant pressure. \( \theta \) is the temperature a parcel of dry air with actual temperature \( T \) would have if it was expanded or compressed adiabatically to \( p_0 \). With (E.1) it follows that

\[ T \cdot \frac{\partial \ln \theta}{\partial z} = \frac{g}{c_p} + \frac{\partial T}{\partial z} \]

If the negative vertical temperature gradient \( -\frac{\partial T}{\partial z} \) (laps rate) is smaller than the adiabatic laps rate \( \frac{g}{c_p} \), the potential temperature monotonically increases with height. This is generally the case for the atmospheric temperature profiles, and thus \( \theta \) can be used as a vertical coordinate. The atmosphere is then said to be stably stratified or statically stable. \( \theta \) is closely related to the specific entropy (entropy per unit mass) \( S = c_p \ln \theta + S_0 \), and surfaces of constant potential temperature are isentropic levels. As middle atmospheric processes on time scales of several days are nearly adiabatic, \( \theta \) is a useful vertical coordinate. Adiabatic flows of air parcels take place along isentropic surfaces, but of course not all atmospheric processes are adiabatic. Important deviations arise from radiative effects or from release of latent heat. Using the first law of

<table>
<thead>
<tr>
<th>Characteristic quantity</th>
<th>Temperature</th>
<th>Composition</th>
<th>Plasma</th>
<th>Magnetic field</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁵</td>
<td></td>
<td>Geocorona</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁴</td>
<td></td>
<td>Heterosphere</td>
<td></td>
<td>Plasmapause</td>
</tr>
<tr>
<td>1000</td>
<td></td>
<td>Homopause</td>
<td></td>
<td>Plasmasphere</td>
</tr>
<tr>
<td>100</td>
<td>Thermosphere</td>
<td></td>
<td>F-Region</td>
<td>Magnetopause</td>
</tr>
<tr>
<td>10</td>
<td>Mesosphere</td>
<td>Heterosphere</td>
<td></td>
<td>(Sun direction)</td>
</tr>
<tr>
<td>10</td>
<td>Stratosphere</td>
<td></td>
<td>E-Region</td>
<td>Plasmapause</td>
</tr>
<tr>
<td>0</td>
<td>Tropopause</td>
<td>Homosphere</td>
<td></td>
<td>Plasmapause</td>
</tr>
<tr>
<td></td>
<td>Tropopause</td>
<td></td>
<td></td>
<td>Magnetopause</td>
</tr>
</tbody>
</table>

Figure 2.5: Vertical classification of the Earth’s atmosphere, and its near-space environment, motivated by Prölls [2001].
thermodynamics, the rate of $\theta$ change along an air parcel’s trajectory is

$$\frac{d\theta}{dt} = \left[\frac{p_0}{p}\right]^{\kappa} \frac{Q}{c_p}$$

where $Q$ denotes the net heating rate per unit mass. Processes which alter the potential temperature of an air parcel are called diabatic.

The atmosphere is usually divided into four layers according to the mean vertical temperature profile (figure 2.6). In the lowermost part, the troposphere, the temperature generally decreases with height up to a minimum called the tropopause. Above that, stratosphere, mesosphere, and thermosphere follow; the boundaries between them are called stratopause, and mesopause. The temperatures, their gradients within the layers, and the locations of the boundaries, especially the height of the tropopause, vary with season and latitude [Brasseur and Solomon, 2005].

The region between tropopause and homopause is commonly referred to as the middle atmosphere. It contains the bulk of atmospheric ozone and is the level at which solar energetic protons lose most of their energy and is therefore the region of main interest for this study. The distribution of the chemical species in the middle atmosphere depends on photochemical reactions as well as on dynamical processes. An important global scale atmospheric transport pattern is the so called Brewer-Dobson circulation which describes the mean meridional atmospheric flow. Thermal convection in the troposphere is strongest at low latitudes, and ascending air masses enter the tropical and subtropical stratosphere. From there poleward motions transport air to mid and high latitudes in both hemispheres where subsidence into the troposphere
takes place. At higher altitudes another characteristic flow structure occurs around the solstices: There is upper stratospheric and mesospheric upward motion in the summer hemisphere driven by solar insulation, summer to winter motion in the mesosphere, and descent over the winter pole (figure 2.7). These meridional flows are very important for the transport of trace gases between different climatic regions. The meridional circulation differs in northern and southern hemisphere. Because of differences in orography and land-ocean coverage, there is stronger planetary wave activity during winter in the northern hemisphere than in the southern hemisphere. This leads to a stronger Brewer-Dobson circulation in the northern midwinter than during the southern midwinter.

The pronounced latitudinal temperature differences give rise to pressure gradient forces which are on large scales basically balanced by coriolis forces of zonal flows. The resulting mean zonal winds are much stronger than the averaged meridional winds, but they are conceptually less important in terms of global transport of chemical species. Important exceptions are the so called polar vortices in both hemispheres: Strong zonal winds occur especially in the sub-polar region in the winter hemisphere. As a result there are persistent large-scale cyclonic circulations generally centred in the polar winter region. Such a polar vortex seals the encapsulated air masses against meridional inflow, and also weakens the heat flux into the polar regions, especially during winter. The Antarctic polar vortex is much more pronounced than its Arctic counterpart which is disturbed by topography. As a result, temperatures in the southern polar vortex get much colder than in the Arctic vortex.

2.4.2 The ozone layer

The bulk of atmospheric ozone (O$_3$) is located in the lower stratosphere between approximative 15 km and 35 km. This structure is commonly called the stratospheric ozone layer. Its thickness and height vary seasonally and geographically. A first attempt to explain the characteristic atmospheric ozone concentrations was made by Chapman [1930] who considered only oxygen reactions. Basically all ozone in the atmosphere is formed by

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]  

(2.1)
M is an arbitrary molecule which is required to satisfy conservation of energy and momentum in that reaction, typically it is N\textsubscript{2} or O\textsubscript{2}. An important source of atomic oxygen in the middle atmosphere is the photodissociation of molecular oxygen by ultraviolet radiation at wavelengths less than 242.2 nm:

\[ O_2 + h\nu \rightarrow 2O \quad (2.2) \]

The released oxygen atoms are in ground state (\(^3\text{P}\)) for wavelength larger than 175.9 nm, below this limit also O(\(^1\text{D}\)) is produced. There is photolysis of ozone as well,

\[ O_3 + h\nu \rightarrow O + O_2 \quad (2.3) \]

in principle possible for wavelengths smaller than 1123 nm, but most pronounced in the wavelength interval from 230 nm to 320 nm where O(\(^1\text{D}\)) is released. Another sink for ozone is the recombination

\[ O_3 + O \rightarrow 2O_2 \quad (2.4) \]

This set of reactions constitutes the Chapman cycle. As a result of the rapidity of the reactions (2.1) and (2.3) under daylight conditions, O\textsubscript{3} and O are effectively interconverted in the stratosphere. Therefore it is useful to think of the sum of ozone and atomic oxygen as a single species, called odd oxygen: \(O_x=\{O_3, O(\(^3\text{P}\)), O(\(^1\text{D}\))\}\). Chapman’s reactions qualitatively explain the existence of the ozone layer but the predicted stratospheric ozone concentrations are too large compared with the empirical data. The main reason for this is that the pure oxygen chemistry of the Chapman cycle does not account for ozone depletion by other atmospheric substances. Of great importance are catalytic cycles of the form

\[ X + O_3 \rightarrow XO + O_2 \]
\[ XO + O \rightarrow X + O_2 \quad (2.5) \]

The net effect of this is the same as of reaction (2.4). X is a free radical catalyst, e.g. H, OH, NO, Cl or Br. There are several other interlinked odd oxygen destroying reactions involving nitrogen, hydrogen, and halogen species, see for instance Wayne [2000]. Due to the rapid interconversions of related species, the “families” \(HO_x=\{H, OH, HO_2\}\), \(NO_x=\{N, NO, NO_2\}\), \(ClO_x=\{Cl, ClO, 2\times Cl_2O_3\}\), and \(BrO_x=\{Br, BrO\}\) are useful entities in the stratosphere. They are used in atmospheric modelling (section 3.2). Lary [1997] gives a comprehensive survey of the effectiveness of different catalytic cycles in destroying ozone in the stratosphere. The \(HO_x\) caused O\textsubscript{3} destruction is very effective in the upper part of the middle atmosphere, and the effectiveness of \(NO_x\) is highest in the upper stratosphere. This will be of importance for the chemical impacts caused by solar proton events. The anthropogenic increase of atmospheric ClO\textsubscript{x} and BrO\textsubscript{x} is mainly responsible for the ozone hole phenomena and for ozone loss at mid latitudes. Besides the photo-chemistry it is the atmospheric transport patterns which control the ozone content in the middle atmosphere. Rates of O\textsubscript{3} production are highest at about 40 km altitude in the tropics. The stratospheric lifetime of ozone molecules is long enough that they can be transported over global distances. Due to the Brewer-Dobson circulation, O\textsubscript{3} is carried from the equator to the poles typically within 3 to 4 month.

### 2.4.3 Some aspects of ion chemistry

Most of the atmospheric constituents are electrical neutral, but charged molecules and atoms together with free electrons play a substantial role in the middle and upper atmosphere. The main atmospheric ionisation sources are shortwave solar radiation (extreme UV and X-rays),
and the energetic charged particles (mainly electrons and protons) of solar and cosmic origin which penetrate into the atmosphere. The latter are also called galactic cosmic rays (GCRs). The atmospheric region with significant concentrations of ions of thermal energy is called the ionosphere. It can be divided into a number of characteristic layers (figure 2.5) according to the mean vertical profile of electron density (figure 2.8). The D-region is located between about 60 to 90 km. Here the ions are mainly produced by photoionisation of nitric oxide by Lyman-α radiation at 121.6 nm. Additionally, high energetic GCRs contribute to the ionisation of N₂ and O₂ below about 70 km. The following E-region extends up to an altitude of approximative 130 km. In this layer, X-rays and Lyman-β (102.6 nm) are the main ionisation sources of atomic oxygen, O₂, and N₂. In the F-region, above 130 km, ionisations result mostly from photoionisation of O and N₂. The different ionisation sources and their properties will be considered in more detail in section 6 for the purpose of an ion chemistry model.

The diatomic nitrogen ions undergo rapid charge exchange reactions

\[
\begin{align*}
N_2^+ + O_2 &\rightarrow N_2 + O_2^+ \\
N_2^+ + O &\rightarrow N_2 + O^+
\end{align*}
\]

and are therefore effectively removed. The diatomic oxygen ions can react with N₂:

\[
O_2^+ + N_2 \rightarrow NO + NO^+
\]

The associated reaction coefficient is rather small, but due to the large abundance of N₂, this is an important process in D-region and E-region. NO⁺ is also formed by O₂⁺ + NO → O₂ + NO⁺. As a result, the main ionic constituents in the E-region are O₂⁺, NO⁺, and electrons. The situation in the D-region is much more complex because in the presence of water vapour O₂⁺ and NO⁺ are transferred to proton hydrates H⁺(H₂O)ₙ, and other cluster ions such as H⁺(H₂O)(OH), NO⁺(H₂O), NO⁺(N₂), NO⁺(CO₂), etc. At the same time, electron attachment to molecules of high electron affinity, e.g. oxygen compounds, produce molecular anions. In the D-region, their concentrations exceed the electron concentrations. A general introduction to ionospheres is given, for example, by Bauer [1973], whilst, for instance, Wayne [2000] and Brasseur and Solomon [2005] address more specifically aspects from the atmospheric point of view.

A complex set of rapid reactions relates the ions with uncharged species, and influences the neutral chemistry. Interesting for the purpose of this study are especially the reactions which release NOₓ. Some of the most important, besides (2.7), are:

\[
\begin{align*}
NO^+ + e &\rightarrow O + N \\
O^+ + N_2 &\rightarrow NO^+ + N \\
N^+ + O_2 &\rightarrow O_2^+ + N \\
N_2^+ + O &\rightarrow NO^+ + N \\
N_2^+ + e &\rightarrow N + N
\end{align*}
\]

The nitrogen atoms resulting from these processes are mostly in the ground state (⁴S) and the first electronic excited state (²D). In the middle atmosphere, almost every N(²D) reacts rapidly with O₂, producing NO + O. On the other hand, N(⁴S) + O₂ → NO + O is relatively slow, and most of N(⁴S) is instead destroyed by

\[
N(⁴S) + NO \rightarrow N_2 + O
\]

This removes two NOₓ particles. Therefore, the net NOₓ production of the reactions (2.8) depends very significantly on the branching ratios of N(⁴S) and N(²D), see e.g. Rusch et al.,
2.4.4 Atmospheric impacts of energetic charged particles

After energetic charged solar particles or GCRs have entered the atmosphere, they lose kinetic energy through collisional interactions with air molecules, and a number of partly ionised atomic and molecular fragments is produced. The particles’ energies generally lie below the limits for nuclear interactions [Reid 1976]. How far the particles penetrate into the atmosphere depends on their energy and mass. Figure 2.9 shows atmospheric energy loss profiles for protons having several MeV (about 1 GeV is needed to reach the Earth’s surface). It also displays that the protons lose most of their energy at the end of their ways through the atmosphere. The energetic protons and heavier nuclei are just weakly deflected during their interactions with air molecules and atoms, and their paths are almost straight. Electrons show a different behaviour, due to their smaller mass they experience pronounced deflections resulting in zigzag paths, and usually do not reach very deep down into the atmosphere. This is an important reason for the smaller atmospheric impacts of energetic solar electrons in comparison with protons.
2.4. The Earth’s Atmosphere

[Steinhilber, 2005], and the justification for using the term solar proton events. Due to the large atmospheric abundance of molecular nitrogen and oxygen, initially mainly $\text{N}_2^+$, $\text{O}_2^+$, $\text{N}^+$, $\text{O}^+$, and atomic oxygen and nitrogen are produced along the proton’s flight paths. Energetic secondary electrons cause further dissociations and ionisations [Porter et al., 1976, and Rusch et al., 1981]. Large SPEs can cause significant disturbances of the ionosphere’s D-region [Swider et al., 1978]. Through the rapid reactions indicated in section 2.4.3, reactive $\text{NO}_x$ and $\text{HO}_x$ are produced. As described in section 2.4.2, both $\text{NO}_x$ and $\text{HO}_x$ can destroy ozone in catalytic cycles. Furthermore there is atomic oxygen released [Porter et al., 1976] which directly affects the odd oxygen chemistry. As a result, the ozone chemistry can be significantly disturbed by SPEs. Because of their high reactivity, the produced $\text{HO}_x$ species have a relatively short lifetime, and transport processes are of minor importance for them. In contrast to that, enhanced $\text{NO}_x$ concentrations can remain on high levels for several weeks or even month after a SPE, provided that destruction through photolysis is small. This is especially the case under polar night conditions which at the same time cause pronounced transport by descending air masses. These dynamical issues in combination with the longer lifetimes at high solar zenith angles enable $\text{NO}_x$ to be transported downward quite effectively (Jackman et al., [1990], Randall et al., [2000]) and to cause significant upper stratospheric ozone depletions months after an event [Jackman et al., 2000]. In various studies the impacts of several large SPEs on the middle atmosphere have been analysed. The formation of $\text{NO}_x$ and the subsequent $\text{O}_3$ destruction have been measured during a number of large SPEs and the findings are in accordance with results from atmospheric chemistry models [e.g. Solomon et al., 1983; Jackman et al., 2001; Verronen et al., 2005; Rohen et al., 2005].

![Figure 2.9: Calculated specific energy loss for protons of different initial energies as a function of altitude, adapted from Quack [2001].](image)
3. The atmospheric model

There is a variety of atmospheric models designed for different purposes. An introduction to atmospheric simulations and a classification of different models is for example to be found in the textbooks of Seinfeld et al. [1998] and Brasseur et al. [1999], and basic aspects of physical modelling in general are addressed by Huttner and Jöhnk [2004]. With the equation of continuity in mind, there are basically two classes of processes which alter the chemical composition at a given location, namely transport (advective, diffusive, and convective) and conversion of substances (through phase transitions and photochemical reactions). The latter generally control the evolution of the different species in a given volume in the middle atmosphere on shorter time-scales (minutes up to days). Transport of chemicals (and heat) has to be taken into account if longer time periods and global connections are of interest. For the SPE-caused ozone destructions, atmospheric transport processes are of great importance. In particular, the subsidence of NO\textsubscript{x} in the winter hemisphere is crucial. Therefore in this study a coupled chemistry and transport model is used. Fortunately, the different timescales of transport and chemistry allow to separate them conceptually, and the chemical model can be executed while the atmospheric dynamics is “frozen”.

3.1 Meteorology

The atmosphere can be regarded as a fluid of small viscosity moving in a rotating frame of reference of nearly spherical geometry. The corresponding equations of motion are well known, but in their most general form they are far more complicated than necessary for a description of the large scale atmospheric motions. Additionally, a proper description of the turbulent nature of fluid motions is very demanding, see for instance Herwig [2002]. Usually several approximations are made to yield the so called primitive equations which govern atmospheric dynamics. This set of equations expresses momentum balance in horizontal directions, hydrostatic balance in the vertical, continuity of mass, and radiative heating, for details see Holton [2004]. For the purpose of this study the meridional transport is of main interest, and therefore it is appropriate to utilise a two-dimensional model which accounts for the atmosphere in a zonally averaged manner. Such models are suitable tools to simulate the dynamical processes in the middle atmosphere, where the conditions are more homogeneous than in the troposphere [Brasseur et al., 1999]. Each considered quantity \( x \) is represented by its longitudinal mean value

\[
\bar{x}(\phi, z) = \frac{1}{2\pi} \int_0^{2\pi} x(\lambda, \phi, z) \, d\lambda
\]

where \( \lambda \) and \( \phi \) denote the degree of longitude and latitude, respectively. \( z \) stands for a vertical coordinate. Any quantity then can be written as the sum of the mean value and a deviation
function: \( x(\lambda, \phi, z) = \bar{x}(\phi, z) + x'(\lambda, \phi, z) \). The deviations give rise to additional terms in the zonally averaged primitive equations which do not constitute a closed system any more. In analogy with the situation of the Reynolds-averaged Navier Stokes equation (e.g. Herwig [2002]), the deviations are also called eddies. They can be related to large scale atmospheric waves [Holton, 2004], and have to be prescribed or calculated with additional assumptions in the model. The zonally averaged set of primitive equations is e.g. given by Andrews et al. [1987].

The model which is used in this study is THIN AIR [Kinnersley, 1996], a two-dimensional dynamical code which calculates zonally averaged temperature and pressure fields, and the transport of the chemical species on a grid of 29 isentropic and 19 latitudinal levels. The corresponding vertical resolution is about 3 km up to approx. 100 km height, and the latitudinal resolution is 9.47°. THIN AIR solves a set of dynamical equations related to the primitive equations, and accounts for the effects of three interacting planetary waves. It has a gravity wave scheme and parametrisations for the eddy fluxes. A detailed description is given by Kinnersley [1996]. The model’s transport time step is 3h. The surface temperature is held at a seasonally varying value, simply parametrised with the atmospheric CO\(_2\) content. Diabatic heating rates are calculated by considering 1) heating due to absorption of shortwave solar radiation by O\(_3\), O\(_2\) and NO\(_2\); 2) heating caused by infrared absorptions of H\(_2\)O, CO\(_2\), CH\(_4\), and N\(_2\)O; and 3) cooling due to longwave emissions of H\(_2\)O, CO\(_2\), and O\(_3\).

### 3.2 Photochemistry

In interaction with the transport processes, photochemical reactions control the abundance of the atmospheric constituents. The atmosphere’s chemistry is dominated by bimolecular and trimolecular reactions as well as photodissociations:

\[
\begin{align*}
A + B & \rightarrow C + D \quad (3.10) \\
A + B + M & \rightarrow C + D + M \quad (3.11) \\
A + h\nu & \rightarrow C + D \quad (3.12)
\end{align*}
\]

For instance, the Chapman cycle in section 2.4.2 includes all of these reaction types. The atmospheric chemical reactions are enframed by emissions, depositions, and rainout. Escape to outer space and the entry of meteorites generally only play a role in the upper atmosphere. As the molecule M is not chemically changed, it is reasonable to consider trimolecular reactions as pseudo-bimolecular, and to account for the dependence on M in the reaction rates. This simplifies the numerical formulation.

Chemical processes in the atmosphere are not necessarily gas-phase reactions. An important aspect of the polar chemistry which leads to ozone hole situations are heterogeneous reactions which take place at the surfaces of polar stratospheric clouds [Solomon, 1999, and references therein]. The net effect of such reactions can be written in the form of reaction (3.10). Under the assumption that the whole chemistry is of the form (3.10) and (3.12), the collectivity of linked chemical reactions translates into a set of coupled quadratic ordinary differential equations of first order. Let \([x_i]\) denote the concentration (e.g. molecules per cm\(^3\)) of the chemical species \(x_i\) (\(i = 1 \ldots N\)). Its rate of change is

\[
\frac{d[x_i]}{dt} = f_i([x_1], \ldots, [x_N]) = P_i - L_i \quad (E.2)
\]
with the production and loss rates
\[
P_i = \sum_{j, m \neq i} k_{jm}[x_j][x_m] + \sum_{m \neq i} j_m[x_m]
\]
\[
L_i = [x_i] \left( \sum_m k_{im}[x_m] + j_i \right)
\]
(E.3)

where \(k_{ij}\) denote the reaction rate coefficients for the (pseudo-)bimolecular reactions, and \(j_i\) the coefficients for the photolysis reactions, with units \((\text{molecules s}^{-1})\) and \(s^{-1}\), respectively. For the atmospheric species of interest, the rates of change differ by orders of magnitude. This makes the set of differential equations a so called stiff system which requires high accuracy when it is numerically integrated. The photochemical model being used in this study is SLIMCAT \([\text{Chipperfield, 1999}]\). It offers different integration methods for the fast reacting species, of which the default SIS scheme has been applied.

### 3.2.1 The Semi-implicit symmetric (SIS) integration

This method is a linearised version of the basic semi-implicit Euler integration to numerically solve (E.2), under the consideration of (E.3). It was developed by \textit{Ramaroson} [1989].\(^2\) The SIS scheme approximates the concentration changes within a timestep \(\Delta t\) implicitly by

\[
\Delta x = x(t + \Delta t) - x(t) \simeq \frac{\Delta t}{2} \left[ f(x(t + \Delta t)) + f(x(t)) \right]
\]

(E.4)

with \(x\) and \(f\) being the tuple of all the \([x_i]\) and \([f_i]\), respectively, according to (E.2). Using the linear approximation \(f(x(t + \Delta t)) \simeq f(x(t)) + df(x(t))/dt \cdot \Delta t\), and the chain rule, this becomes

\[
\Delta x \simeq \frac{\Delta t}{2} \left[ 2f(x(t)) + J_f \Delta x \right]
\]

(E.5)

where \(J_f\) denotes the Jacobian matrix of \(f\). So far this applies to any arbitrary differentiable function \(f\). In the case of the chemical system, \(f\) consists of the production and loss terms of the form (E.3), and can be written as a sum of two functions \(f_1\) and \(f_2\), of which \(f_2\) represents the production and loss rates due to bimolecular reactions, and \(f_1\) the photolysis reactions. \(f_2\) is homogeneous of degree two, that is \(f_2(\lambda x) = \lambda^2 f_2(x)\). And the photolysis reactions lead to terms which are linear (homogeneous of degree one), \(f_1(\lambda x) = \lambda f_1(x)\). Euler’s homogeneous function theorem states that \(f(x) = h^{-1} J_f x\), where \(h\) is the degree of homogeneity of \(f\). It follows that

\[
\Delta x \simeq \frac{\Delta t}{2} \left[ J_{f2} x(t + \Delta t) + 2 J_{f1} x(t + \Delta t) - J_{f1} \Delta x \right]
\]

(E.6)

the last term on the right side is proportional to \(\Delta t \Delta x\), and in this sense “quadratically small”. It is neglected in the SIS scheme. Therefore one ends with

\[
x(t) \simeq \begin{bmatrix} 1 - \frac{\Delta t}{2} J_{f2} - \Delta t J_{f1} \end{bmatrix} x(t + \Delta t)
\]

(E.7)

---

\(^2\)The delineation of the SIS in this section is not based upon Ramaroson’s French article, and it might differ from his original derivation.
Table 3.1: The chemical species in the SLIMCAT model.

<table>
<thead>
<tr>
<th>Short lived species</th>
<th>Long lived species</th>
<th>Steady state</th>
<th>Fixed</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O_x (= O_3 + O(^3P) + O(^1D)) )</td>
<td>( \text{CH}_4, \text{N}_2\text{O}, \text{CO, H}_2\text{O}, \text{CFCl}_3, \text{CF}_2\text{Cl}_2, \text{CH}_3\text{Cl}, \text{CH}_3\text{CCl}_3, \text{CCl}_4, \text{CH}_3\text{Br}, \text{CBrClF}_2, \text{CBrF}_3, \text{COF}_2, \text{COFCl, HF} )</td>
<td>( \text{H, OH, HO}_2, \text{CH}_3, \text{CH}_3\text{O}_2, \text{CH}_3\text{O}, \text{HCO, CH}_3\text{OOH} )</td>
<td>( \text{N}_2, \text{O}_2, \text{H}_2 )</td>
</tr>
<tr>
<td>( \text{NO}_x (= N + \text{NO} + \text{NO}_2) ), ( \text{ClO}_x (= \text{Cl} + \text{ClO} + 2 \times \text{Cl}_2\text{O}_2) ), ( \text{BrO}_x (= \text{Br} + \text{BrO}) ), ( \text{HCl, HOCl, OClO, ClONO}_2, \text{HBr, HOBr, BrCl, CH}_2\text{O, NO}_3, \text{N}_2\text{O}_5, \text{HNO}_3, \text{HO}_2\text{NO}_2, \text{H}_2\text{O}, \text{BrONO}_2 )</td>
<td>( \text{H}_2\text{O} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In order to calculate \( x(t + \Delta t) \) from the given \( x(t) \), the matrix \( M \) has to be inverted. This has to be done at all of the model's grid points for each time step along the course of model time. At each step, the entries of \( M \) have to be set according to the local chemical and thermodynamic state. SLIMCAT uses the Gaussian elimination method to invert \( M \). This is by far the most time-consuming part of the program.

3.2.2 The chemical scheme

SLIMCAT considers 53 chemical species. According to their different reactivities, they are assigned to four groups (table 3.1), and treated in different ways. The molecules \( \text{N}_2, \text{O}_2, \) and \( \text{H}_2 \) are well mixed in the homosphere. Their concentrations (molecules/volume) are assumed to vary only with air density, thus they are determined by the meteorology. The other chemical species considered change their local concentrations through photochemical reactions but they do it on different timescales. Only the short-lived species are SIS integrated while for the long lived species the less time consuming simple forward-Euler method is used. In order to save computing time, SLIMCAT does not integrate closely coupled species independently but treats them in “families”. For instance, \( \text{O}_3, \text{O}(^3\text{P}), \) and \( \text{O}(^1\text{D}) \) are combined to form the pseudo-species \( \text{O}_x \) (odd oxygen). The ratios of the species within a family are determined by assuming steady state conditions. This is justified by the fact that the family members are interconverted on timescales shorter than that over which other concentrations vary, and it is therefore a commonly used approach in atmospheric chemical modelling, see e.g. Wayne [2000]. It enables a moderate integration time-step of 15 minutes, and it reduces the dimension of \( M \), compared to a fully independently resolved chemistry. For further details see the description of the chemistry code by Chipperfield [1996].

The assumption of rapid interconversions among certain chemical species which justifies the family approach is reasonable in the troposphere and the stratosphere (for which SLIMCAT was designed), but it does not apply for the upper part of the middle atmosphere. Here the steady state concept in general is not valid. The model had been modified in order to provide suitable simulations of the mesosphere. A version which no longer uses the family concept, and treats water vapour as a short-lived species had already been developed. Table 3.2 lists the modified set of species. This “non-family” version requires a smaller integration step (typically 1 to 5 minutes) than the original SLIMCAT to resolve the evolution of all the reactive species properly. The smaller time step in combination with the larger dimension of the SIS matrix \( M \) makes
3. The atmospheric model

Table 3.2: The chemical species in the non-family SLIMCAT model.

<table>
<thead>
<tr>
<th>Short lived species</th>
<th>O$_3$, O($^3$P), O($^1$D), N, NO, NO$_2$, Cl, ClO, Cl$_2$O$_2$, Br, BrO, HCl, HOCI, ClONO$_2$, HBr, HOBr, BrCl, CH$_2$O, NO$_3$, N$_2$O$_5$, HNO$_3$, HNO$_4$, HO$_2$NO$_2$, H$_2$O$_2$, BrONO$_2$, H, OH, HO$_2$, CH$_3$O$_2$, CH$_3$O, HCO, CH$_3$OOH, H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long lived species</td>
<td>CH$_4$, N$_2$O, CO, CFCl$_3$, CF$_2$Cl$_2$, CHF$_2$Cl, C$_2$F$_3$Cl$_3$, CH$_3$Cl, CH$_3$CCl$_3$, CCl$_4$, CH$_3$Br, CBrClF$_2$, CBrF$_3$, COFCl, HF, COF$_2$</td>
</tr>
<tr>
<td>Fixed</td>
<td>N$_2$, O$_2$, H$_2$</td>
</tr>
</tbody>
</table>

this chemical model rather time consuming. Because of this, it had as yet only been used for simulations of one-dimensional vertical stripes of the atmosphere, without considering transport from and to neighbouring regions, as well as vertical flows. It is a useful tool for the modelling of chemical processes on timescales of several days.

3.2.3 Reaction rates

A detailed description of SLIMCAT, the included reactions, and the model’s treatment of heterogeneous reactions is given by Chipperfield [1999]. The temperature and pressure dependent reaction coefficients utilised by the model have been updated to the JPL [2006] recommendations. In order to calculate the photolysis rates, SLIMCAT uses a radiation transfer scheme which accounts for multiple scattering, and reflection from the Earth’s surface in a two-dimensional spherical geometry up to a solar zenith angle of 98°. The basic input data are a mean solar spectrum, surface albedo, and absorption cross sections of the chemical species. The radiative scheme calculates wavelength dependent radiation enhancement factors from which in turn the local photolysis rates of the different species are derived. Absorption cross sections and quantum yield coefficients are also based on JPL [2006].

3.2.4 Solar proton events

In order to simulate the atmospheric chemical impacts of SPEs, the initial disturbances by the precipitating particles have to be described. An appropriate starting point for the consideration of SPEs are the measured energy dependent particle fluxes provided by satellites such as the Geosynchronous Operational Environmental Satellites (GOES) run by the National Oceanic and Atmospheric Administration Office of Satellite Operations (NOAA) and the Interplanetary Monitoring Platform (IMP-8). From these data atmospheric ionisation rates as a function of time and altitude during a SPE can be derived. A commonly used method is to calculate the particles’ energy losses along their paths in the atmosphere and to use these energy deposition values in a second step to obtain the local ionisation rates, see e.g. Frederick [1976], and Vitt and Jackman [1996]. Finally, the ionisations have to be translated into impacts on the neutral chemistry. The ion pair production rates (IPRs) which are used in this study originate either from calculations based on the Bethe-Bloch formular (Bethe [1930] and Bloch [1933]) which is described
in textbooks such as Porh et al. [1999], or from more sophisticated Monte Carlo simulations using the GEANT-4 code [Agostinelli et al., 2003]. In both cases the secondary ionisations by energetic electrons are considered. The Monte Carlo method is described in detail by Schröter et al. [2005]. Steinhilber [2005] has compared the results from both methods. For protons there are considerable differences at high and low altitudes, but in the relevant atmospheric height region where the bulk of energy deposition takes place the variations are small. The Monte Carlo simulations allow the consideration of electrons as well, but for typical SPE conditions their contribution to the IPRs is quite small [Steinhilber, 2005]. As such, for SPEs the IPRs from both the Bethe-Bloch calculations as well as from the Monte Carlo simulations can be used.

There are basically two ways of translating the IPRs into effects on the neutral chemistry. Either the ion chemical reactions in interplay with neutrals can be simulated in detail or simple parametrisations can be used. The former approach will be addressed in section 6, the latter here. Studies on the effects of energetic particle precipitation (e.g. by Porter et al. [1976], Rusch et al. [1981], and Solomon et al. [1981]) have provided parametrisations which allow the calculation of approximative production rates for NO$_x$, HO$_x$, and atomic oxygen for a given IPR. This method has been widely used e.g. by Jackman et al. [2000, 2001, and 2005a+b] and Sinnhuber et al. [2003]. The results generally correspond well with observed chemical perturbations due to SPEs, especially ozone destruction, e.g. Rohen et al. [2005], and it has the clear advantage of not causing any significant computational burden. For this study a similar parametrisation has been used which will hereafter be referred to as the standard parametrisation. It is described in the following section.

### 3.2.5 Standard production factors for NO$_x$, HO$_x$ and O

Following Porter et al. [1976], NO$_x$ formation is set to be 1.25 molecules per ion pair produced, and the branching ratio between N($^4$S) and N($^2$D) is 45% : 55%. As mentioned in section 2.4.3, N($^2$D) rapidly reacts via N + O$_2$ → NO + O; in the model it is therefore assumed that N($^2$D) instantaneously becomes NO and the same amount of atomic oxygen is released. The chosen numbers are in accordance with the values given by Rusch et al. [1981], and they are also used e.g. by Semeniuk et al. [2005].

Due to the complex water ion-cluster chemistry (section 2.4.3), the production factors for HO$_x$ depend on water concentrations as well as on several other parameters such as the abundance of atomic oxygen. The simplified reaction scheme delineated by Solomon et al. [1981] is used to calculate these factors depending on the concentrations provided by SLIMCAT. The production factors are very similar to the values used by Jackman et al. [2005a]. The HO$_x$ production per ionisation is nearly one H + OH below about 50 km (resulting from water depletion, reaction 2.10 in section 2.4.3) but decreases significantly with height. An according loss of water molecules is implemented in the model. Finally, the direct release of atomic oxygen is assumed to be 1.15 atoms per ion pair produced [Porter et al., 1976].

Some critical remarks concerning the process chain from measured energy spectra to production rates of reactive neutrals are necessary. The first issue is the calculation of IPRs from the energy loss profiles. For this purpose a mean ionisation energy has to be assumed. From the Fermi-Thomas model (see e.g. textbooks like Allkofer [1971]) the mean electron binding energy in a N$_2$ and O$_2$ mixture with atmospheric abundances can be estimated to be approximative 95 eV. But this neglects the fact that outer electrons are more likely to be removed from the molecules than the ones from inner shells. Additionally, it does not account for the effects of ionisations by secondary electrons, and molecular excitations. Empirically, a value of 35 eV has been derived by Porter et al. [1976] which is used e.g. by Callis et al. [1998] and Jackman et al. [2000],
and is also adapted in the IPR calculations for this study. The questionable point with this empirical value is that it was obtained by considering a certain energy interval of protons. Since then the measured proton’s energy range has been expanded which could imply that the IPRs are overestimated. Also the next step, the calculation of NO\textsubscript{x}, HO\textsubscript{x} and O production from the IPRs, includes empirical assumptions, for example the branching ratio between dissociative and non-dissociative ionisation of N\textsubscript{2} by secondary electrons is not known from first principles but has been adjusted to match with observations. Furthermore the fraction of nitrogen atoms which are released in excited state is also not known unambiguously. For both issues see for instance Rusch et al. [1981]. It should be emphasised and kept in mind that the SPE production rates of the reactive neutrals have been tuned in order to satisfy a rather limited set of measurements, and that there are some uncertainties.
4. Model developments during the thesis I: Neutral chemistry

4.1 The hybrid model

For the purpose of a proper simulation of the whole middle atmosphere, a hybrid chemical scheme has been developed. It uses the family approach where it is appropriate, basically in the stratosphere and lower mesosphere, whereas the non-family concept is applied for the upper region. The transition height between the two regimes can be chosen arbitrarily. Therefore the model can be used as a pure family version, as a non-family version, or as any intermediate combination. Typically the non-family treatment was set to start at the vertical level of \( \theta = 2360 \) K which corresponds to an altitude of about 51 km. This choice establishes a reasonable compromise between accuracy and computing demands, and makes the hybrid chemical scheme suitable to be used in the two-dimensional atmospheric model. According to the changed chemistry the coupling to THIN AIR’s transport scheme had to be adjusted. The computing expenses of the hybrid model in this form are roughly 8 times larger than the ones of the original SLIMCAT-THIN AIR combination. Figure 4.1 shows results from both family and hybrid model for water vapour, compared with measurements. The hybrid model is in much better agreement with the measurement data at higher altitudes than the family model.

4.2 Thermospheric nitric oxide

In the thermosphere, photodissociation of N\(_2\) and energetic particle impact are important sources of atomic nitrogen, see e.g. Bailey et al. [2002]. Through N + O\(_2\) \(\rightarrow\) NO + O nitric oxide is formed. This contributes significantly to the NO budget of the lower thermosphere [Brasseur and Solomon, 2005]. Other sources of NO are the reaction of energetic O\((^3\)P) with N\(_2\) [Balakrishnan and Dalgarno, 2003] and excited N\(_2\) reacting with atomic oxygen [Campbell et al., 2007]. Downward transport of thermospheric NO, especially in the winter hemisphere, influence the mesospheric NO content. The original atmospheric model does not account for this. It extends up to an altitude of about 100 km, and photodissociation of N\(_2\) is negligible below that level. The same applies for the reactions O\((^3\)P) + N\(_2\) and N\(_2^*\) + O. The model’s transport scheme balances the total global outflow across the upper boundary with an inflow in regions of downward motions, without considering any sources above. As a result, the model underestimates the NO content in the upper atmospheric layers. In order to get a more realistic picture, the NO abundance in the uppermost model layer is prescribed by the means of measured nitric oxide concentrations from the Student Nitric Oxide Explorer (SNOE) [Barth et al., 2003]. The applied NO concentrations are simply the SNOE measurements at 100 km, for each day of the year, and
Figure 4.1: Water vapour volume mixing ratios at noon on July the 12th simulated by the family and hybrid model in comparison with July mean MLS (Microwave Limb Sounder) data from the UARS (Upper Atmosphere Research Satellite) Reference Atmosphere Project.
4.3. Acetonitril

Acetonitril (CH$_3$CN) is one of the most abundant cyanides in the atmosphere. Typical mixing ratios are around 150 ppt in the troposphere [Singh et al., 2003], showing pronounced local and seasonal variations, and decrease substantially with height in the stratosphere [Arijs and Brasseur, 1986]. Especially in the lower stratosphere, acetonitril is involved in ion cluster chemistry (Brasseur and Chatel [1983]; Arijs and Brasseur [1986]; Beig et al. [1993]). Due to the fact that its dipole moment and its proton affinity exceed the values of the water molecule, it is
able to replace $\text{H}_2\text{O}$ in ionic water clusters:

$$\text{H}_3\text{O}^+(\text{H}_2\text{O})_m(\text{CH}_3\text{CN})_n + \text{CH}_3\text{CN} \rightarrow \text{H}_3\text{O}^+(\text{H}_2\text{O})_{m-1}(\text{CH}_3\text{CN})_{n+1} + \text{H}_2\text{O}$$

($m = 1, 2, \ldots ; n = 0, 1, \ldots$)

This makes CH$_3$CN important for the stratospheric ion chemistry, and therefore it was implemented in the atmospheric model as a preparation for the ion chemistry addressed in section 6. As SLIMCAT is designed mainly for the stratosphere, it misses to treat the complex organic reactions taking place in the troposphere. A pragmatic approach has been chosen using a simplified chemistry scheme to model the CH$_3$CN concentrations without aiming to resolve the whole outfit in the troposphere. It is believed that the bulk of atmospheric CH$_3$CN originates from biomass burning and biogenic emissions, and significant loss rates can be attributed to ocean uptake [Singh et al., 2003]. The same surface sources and sinks apply for the other important cyanide in the atmosphere, the HCN molecule (hydrogen cyanide). The mixing ratios for CH$_3$CN and HCN tend to be correlated in the free troposphere (that is above the boundary layer), see e.g. Li et al. [2000], and Singh et al. [2003]. Earlier suggestions by Murad et al. [1984] that hydrogen cyanide could be a precursor for acetonitril in the atmosphere have not been confirmed. The investigations of Brasseur and Zellner [1985] have shown that HCN is unlikely an atmospheric source of CH$_3$CN. Therefore the atmospheric acetonitril can be modelled without considering any HCN chemistry$^3$. In several studies, it has been shown that it is possible to reproduce the atmospheric abundance of acetonitril above the boundary layer by considering only a set of very basic reactions and sources, e.g. Brasseur et al. [1983], Arijs and Brasseur [1986], and Li et al. [2003]. In a comparable way, CH$_3$CN was included in the model, see table 4.3 for the considered processes. The emissions from biomass burning have a clear diurnal cycle and are highest at low latitudes. In order to at least qualitatively account for their distribution, the CH$_3$CN biomass emissions have been weighted with global fire counting rates (MODIS data) courtesy of Holger Bremer. The other emissions together with ocean uptake are simply equally distributed over the globe. For ocean uptake a rather small value has been applied to obtain reasonable results, see the comment attached to table 4.3. In the troposphere and stratosphere, photodissociation of acetonitril is a much smaller sink than the reactions listed in table 4.3 [Suto and Lee, 1985]. It is therefore not considered. The CH$_3$CN molecule is treated as a long-lived species. Figure 4.3 displays the modelled abundance of acetonitril. The values in the troposphere are generally smaller (about 50 ppt) than the observed mixing ratios [Li et al., 2000, and Singh et al. 2003]. On the other hand, the stratospheric abundance is higher than in the classical simulations [Brasseur et al., 1984, and Arijs and Brasseur [1986], and it is in better accordance with newer models. For instance, the stratospheric concentrations compare fairly well to the ones used by the University of Bern Atmospheric Ion Model [Kazil, 2002].

$^3$More recently, Tyndall et al. [2001] have studied the fate of products from CH$_3$CN oxidation by chlorine atoms and hydroxyl molecules in the laboratory. They found that via the formation of HC(O)CN, and through some longer reaction chains, HCN can be produced. Kleinböhl et al. [2006] yielded better agreements with HCN measurement data when production from CH$_3$CN is taken into account as if it is neglected. Interestingly, this seems to reverse the link between CH$_3$CN and HCN, suggested by Murad et al.. This is intriguing, but the HCN chemistry itself lies outside the scope of this study.
4.3. Acetonitril

Figure 4.3: Modelled acetonitril volume mixing ratios at noon on July the 12th.

Table 4.3: The CH$_3$CN chemistry in the model

<table>
<thead>
<tr>
<th>Sources, sinks and reactions</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total biomass burning source</td>
<td>0.47 Tg(N) yr$^{-1}$</td>
<td>L</td>
</tr>
<tr>
<td>Total coal burning source</td>
<td>0.03 Tg(N) yr$^{-1}$</td>
<td>L</td>
</tr>
<tr>
<td>Total biogenic and other sources</td>
<td>0.2 Tg(N) yr$^{-1}$</td>
<td>S</td>
</tr>
<tr>
<td>Mean ocean deposit velocity</td>
<td>0.01 cm s$^{-1}$</td>
<td>S$^a$</td>
</tr>
<tr>
<td>Tropospheric rainout</td>
<td>$4.5 \times 10^{-8} \exp\left(-\frac{z}{[\text{km}]}^2/15.4\right)$ s$^{-1}$</td>
<td>AB</td>
</tr>
<tr>
<td>CH$_3$CN + OH</td>
<td>$6.28 \times 10^{-13} \exp\left(-1030/T\right)$ cm$^3$s$^{-1}$</td>
<td>KK</td>
</tr>
<tr>
<td>CH$_3$CN + O($^3$P)</td>
<td>$7.27 \times 10^{-13} \exp\left(-2385/T\right)$ cm$^3$s$^{-1}$</td>
<td>AB</td>
</tr>
<tr>
<td>CH$_3$CN + O($^1$D)</td>
<td>$10^{-10}$ cm$^3$s$^{-1}$</td>
<td>AB</td>
</tr>
<tr>
<td>CH$_3$CN + Cl</td>
<td>$1.6 \times 10^{-11} \exp\left(-2140/T\right)$ cm$^3$s$^{-1}$</td>
<td>T</td>
</tr>
</tbody>
</table>

References:  
L Li et al. [2003]  
S Singh et al. [2003]  
AB Arijs and Brasseur [1986]  
KK Kurylo and Knable [1984]  
T Tyndall et al., [1996]

$^a$the value used for the ocean deposit velocity lies at the lower edge of the range being reported on in the literature, see e.g. Singh et al. [2003]. They themselves favour 0.06 cm s$^{-1}$ which leads to unrealistically low CH$_3$CN concentrations when it is used in the simple scheme presented here. This is probably due to the fact that the atmospheric model does not provide a proper representation of the tropospheric boundary layer.
5. Modelled ozone in comparison with observations

As the focus of this study is on ozone, it is advisable to assess the modelled O$_3$ before the impacts of SPEs are approached. The stratospheric ozone mixing ratios are very similar in both the family and the hybrid model, and they agree qualitatively quite well with measurements. A comparison between simulated and measured ozone is shown in figure 5.1. The models predict high O$_3$ mixing ratios in the polar winter mesosphere, a manifestation of the so called secondary ozone maximum which has been first detected in daytime ozone by Evans and Llewellyn [1972], and, more pronounced, during night by Hays and Roble [1973]. While the family model seems to overestimate magnitude and size of that maximum, the hybrid model gives a more realistic picture in the polar winter region, for instance in comparison with the results of Marsh et al. [2001]. In general, the family model tends to yields too high ozone mixing ratios in the upper part of the middle atmosphere. But in terms of the total atmospheric ozone content, this mesospheric contribution is of minor importance. On the other hand, small differences in mixing ratios at lower stratospheric levels correspond to large spreads in the total ozone content.

A suitable measure of the overall atmospheric ozone above a given surface location is the total ozone column

\[ \text{TOC} = \int_{0}^{\hat{z}} [O_3](z) \, dz \]

where [O$_3$](z) is the ozone number density [molecules/volume] at height z. The upper integration limit $\hat{z}$ denotes the “top of the atmosphere”. As the bulk of ozone is located in the stratosphere, for $\hat{z}$ simply the highest model altitude can be used. TOC has the unit molecules/area and is usually expressed in Dobson Units (1 DU=2.69×10$^{16}$ ozone molecules per square centimetre).

The total ozone column is a useful quantity because the absorption of solar UV-B radiation depends, to a good first approximation, linearly on it. Figure 5.2 shows the modelled total ozone column in the southern polar region from winter 2000 to winter 2001. The TOCs of family and hybrid model are very similar, only during polar spring and early summer the TOC reduction due to the ozone hole is a bit smaller in the hybrid model than in the family version.

The ejection of thermospheric nitric oxide in the model does not influence the ozone budget significantly, the O$_3$ volume mixing ratios differ typically by clearly less than 0.5 % and consequently there is no noteworthy impact on the total ozone column.

Figure 5.3 contrasts the modelled TOC with measurement data from the Global Ozone Monitoring Experiment (GOME) [Weber et al., 2005]. In general, the TOC values from the model are larger than the observed TOCs. While the differences are small in the tropics, they increase with latitude in both hemispheres. This overestimation of the total ozone columns is a well known property of SLIMCAT in combination with the THIN AIR model while results from SLIMCAT embedded in a three-dimensional transport model match much better with measured TOCs.
5. Modelled ozone in comparison with observations

Figure 5.1: Modelled ozone volume mixing ratios for July 12th at noon in comparison with measurement data (URAP [2006]).
Figure 5.2: Antarctic (85.3°S) total ozone column in Dobson Units from July 2000 to June 2001 simulated with family and hybrid model, respectively. The ozone dip in the blue interval is the model’s “ozone hole”.

[Chipperfield, 2003]. This is because THIN AIR has the same drawbacks as basically any zonally averaged atmospheric model with fixed horizontal (Eulerian) coordinates. A main reason for the discrepancies of such models is that the concept of eddy diffusion (treated as Fickian diffusion) causes unrealistically strong transport across atmospheric barriers such as the polar vortex and the “surf zone” at mid-latitudes [Nakamura, 2001, and references therein]. As a result, the modelled TOCs in the polar regions are too high, and especially the ozone hole depletions are reproduced rather qualitatively than in terms of absolute numbers. Nevertheless, zonally averaged models have recently still widely been used for the simulation of the atmospheric ozone chemistry, including the polar regions, see for instance WMO [2003]. For the purpose of this study, especially for the long time simulations which are addressed in chapter 9, a two-dimensional model has been the only practical choice. A three-dimensional model would have been much too time consuming. Due to the fact that the total ozone is overestimated by two-dimensional models to quite some extent, usually rather differences and relative variations of the TOC than absolute values are considered, for example in WMO [2003]. Figure 5.4 shows the modelled TOC differences relative to its mean values in comparison with the corresponding GOME data. Though there are some discrepancies between the simulation results and the measured values, especially during polar spring, the SLIMCAT + THIN AIR model is able to reproduce the general seasonal behaviour of the TOC variations fairly well. In this sense it is a suitable simulation tool by which the atmospheric ozone variations can be assessed, but it should be kept in mind that the TOCs themselves are overestimated.
Figure 5.3: The total ozone column during the years 2000 and 2001 in the hybrid model (solid lines) at some selected model latitudes in comparison with GOME data (circles, WFDoas Version 1). The latter are zonally averaged values of the original global data set; in each sub figure all data points are shown which lie inside the latitudinal band around the corresponding model’s latitude.
Figure 5.4: Like figure 5.3 but here the relative variations of the total ozone column with respect to its two year mean value are shown. In case of gaps in the GOME data set (for instance during polar night) the modelled TOC values have not been used for the calculation of the mean.
6. Model developments during the thesis II: The ion chemistry model

Ion chemistry models aim to simulate the composition and properties of the ionosphere in interaction with the neutral chemistry. They can be used to study the perturbations and the subsequent effects on neutral species during single SPEs in detail (e.g. Verronen et al. [2002]), but are quite demanding in terms of computing time. A reasonable field of application regarding SPEs is to re-check the production rates of reactive neutrals.

In this section, a description is given of a model which has been developed for the simulation of the basic atmospheric ion chemistry. For the purpose of this study the impacts of SPE are of main interest, and not the undisturbed ionosphere. On the other hand, it seemed appropriate not to develop a specialised tool which would be restricted to applications of high ionisation rates like under SPE conditions, but rather design a more general model. This allows to investigate interferences between background ion chemistry and disturbances due to precipitating particles, and provides a basis which is prepared for further extensions and future applications. For this study the ion chemistry model is used to calculate SPE production rates for NO$_x$, HO$_x$ and O$_x$.

The results will be described in section 6.4.

The ion chemistry scheme is used in combination with the atmospheric model described in section 4. Thus, it covers basically the D-region and lower E-region of the ionosphere. In this region, effects of non-thermal equilibria are not of very great importance, and therefore neglected. In other words, all reaction products are assumed to be thermalised instantaneously (in terms of kinetic energy, electronic excitations are not affected). The species currently included in the model are listed in table 6.4. The focus is clearly on positive nitrogen, hydrogen, and oxygen compounds. The negative ion chemistry is not resolved, besides electrons there is only the pseudo-species X$^-$ which accounts for all atomic and molecular anions. This is justified because

<table>
<thead>
<tr>
<th>Anions</th>
<th>e, X$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cations</td>
<td>N$_2^+$, N$^+$, O$_2^+$, O$_2^+(a^1D)$, O$^+(2S)$, O$^+(2P)$, NO$^+$, H$^+$, O$<em>3^+$, O$<em>3^+(H_2O)$, H$^+(OH)$, H$^+(H_2O)(OH)$, H$^+(H_2O)</em>{n=1,2...5}$, NO$^+(H_2O)</em>{n=1,2}$, NO$^+(CO_2)$, NO$^+(N_2)$, NO$_2^+(H_2O)$, NO$<em>2^+(CO_2)$, NO$<em>2^+(H_2O)</em>{2}(CO_2)</em>{2}$, NO$_2^+(H_2O)(N_2)$</td>
</tr>
<tr>
<td>Neutrals</td>
<td>N($^4S$), N($^4D$), NO, NO$_2$, H, OH, H$_2$O, N$_2$O$_5$, HNO$_3$, HNO$_2$, O($^3P$), O($^1D$), O$_3$, CH$_3$CN, N$_2$, O$_2$, CO$_2$</td>
</tr>
</tbody>
</table>
the recombination rates of positive with negative species seem not do depend significantly on
the actual carrier of the negative charge, e.g. Arijs and Brasseur [1986].

6.1 Ionisation sources

The starting point for both the ion chemistry as well as for its numerical simulation are the
ion producing processes. Before the SPE ionisations are looked at in section 6.1.3, the other
important sources of atmospheric ions and their treatment in the model are briefly described.

6.1.1 Photoionisations

The most abundant atmospheric species require ionisation energies which correspond to wave-
lengths in the extreme ultraviolet (EUV) or even X-ray regime. An important exception is the
NO molecule. Table 6.5 lists some of the ionisation thresholds for atmospheric molecules. Due
to the fact that such short wavelengths are needed, photoionisations are almost exclusively re-
stricted to the thermosphere and upper mesosphere where strong photoabsorptions take place.
As the Sun’s shortwave output varies significantly with the solar cycle, five reference spectra are
included in the model from which the spectral irradiance for a given day can be interpolated.
Each spectrum consists of a continuous part (5–105 nm, 5 nm resolution) enriched with the 17
most important emission lines. The numerical values are taken from Rees [1999]. A simple ra-
diative scheme is used to calculate the amount of ionising radiation reaching the different model
heights. Optical slant columns in planar spherical geometry are used to calculate the shortwave
extinctions due to absorption by O\textsubscript{2}, O, and N\textsubscript{2} for all solar zenith angles which are not shad-
owed by the Earth. Justified by the strong absorptions in this wavelength regime, scattering is
neglected (the Lyman \(\alpha\) ionisation of NO is treated separately, see below). The concentrations
of O\textsubscript{2}, O, and N\textsubscript{2} are taken from the atmospheric model which only extents up to about 100 km.
In order to consider the absorptions above that height, the pressure value at the edge of the
uppermost model box is used to determine a remaining column, to which the O\textsubscript{2}, O, and N\textsubscript{2}
mixing ratios of the highest model grid point are applied. This estimate neglects the fact that
the relative amount of atomic oxygen increases with height, and finally exceeds the one of O\textsubscript{2},
but for a detailed description a thermospheric model would be required. The calculated spectral
irradiances are then used to yield the photolysis rates.

Table 6.5: Ionisation energies and corresponding threshold wave-
lengths of some important atmospheric molecules and atoms
(taken from Wayne [2000])

<table>
<thead>
<tr>
<th>Species</th>
<th>[eV]</th>
<th>[nm]</th>
<th>Species</th>
<th>[eV]</th>
<th>[nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N\textsubscript{2}</td>
<td>15.6</td>
<td>79.9</td>
<td>O</td>
<td>13.6</td>
<td>91.1</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>15.4</td>
<td>80.4</td>
<td>H</td>
<td>13.6</td>
<td>91.2</td>
</tr>
<tr>
<td>N</td>
<td>14.5</td>
<td>85.2</td>
<td>O\textsubscript{2}</td>
<td>12.1</td>
<td>102.7</td>
</tr>
<tr>
<td>CO</td>
<td>14.0</td>
<td>88.5</td>
<td>NO</td>
<td>9.3</td>
<td>135.0</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>13.8</td>
<td>89.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Photoionisation of O$_2$**

In the wavelength region of interest here, the process

\[ \text{O}_2 + h\nu \rightarrow \text{O}_2^+ + e \]

can either produce a stable O$_2^+$, or can be followed by a rapid dissociation, O$_2^+$ → O + O$^+$ for wavelengths smaller than 61 nm. Whether non-dissociative or dissociative ionisations take place, depends on the molecular O$_2^+$ state excited by the absorbed photon. Measured values for the excitations in the wavelength region between 30.4 and 102.6 nm are given by Rees [1999], these values are used in the model to calculate photoionisations of O$_2$. A st the O$_2^+$ ground state (4S) behaves differently in ionic reactions from the excited states, (2D) and (2P), it is necessary to differentiate between them from their production on. Table 6.6 lists the O$_2^+$ states being excited through photoionisation of O$_2$. There are Rees’ states missing in that table, namely the 2,4Σ$^{-}_g$ and the so called 662˚A-state, which includes all the other dissociative ones. The excitation of 2,4Σ$^{-}_g$ is limited to short wavelengths. A comparison with O$_2^+$ potential curves calculated by Hisosaka et al. [2003] indicates that in the Franck-Condon region 6Σ$^{-}_g$ and 5Σ$^{-}_g$ are likely candidates. The former has the main dissociating products O$^+$(2D) + O(1D). For 5Σ$^{-}_g$ the products are assumed to be O$^+$(2P) + O(3P), and finally, 5Σ$^{-}_g$ is set to contribute with 85% to Rees’ 2,4Σ$^{-}_g$-collection, according to Hisosaka [2003].

The 662˚A is more complicated to decompose, it consists of three broad peaks, the highest energetic one can be related to what Eland and Duerr [1998] have tentatively labelled 4Σ$^{-}_u$ and therefore ends in O$^+$(2P) + O(3P). The other local maxima in 662˚A (around 23.0 eV and 20.3 eV).

<table>
<thead>
<tr>
<th>O$_2^+$ state</th>
<th>Energy$^a$ [eV] above O$_2$ ground state</th>
<th>Dissociation limit [and its energy/eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>X$^2$Π$^g$</td>
<td>12.307</td>
<td>ground state</td>
</tr>
<tr>
<td>a$^4$Π$^u$</td>
<td>16.703</td>
<td>stable</td>
</tr>
<tr>
<td>A$^2$Π$^u$</td>
<td>17.643</td>
<td>stable</td>
</tr>
<tr>
<td>b$^4$Σ$^{-}_u$</td>
<td>18.171</td>
<td>stable$^b$</td>
</tr>
<tr>
<td>B$^2$Π$^{-}_g$</td>
<td>20.296</td>
<td>O$^+$($^4$S)+O(3P)$^c$ [18.73]</td>
</tr>
<tr>
<td>2Π$^{-}_u$</td>
<td>23.900</td>
<td>O$^+$($^2$D)+O(3P) [22.06] and O$^+$($^2$P)+O(3P)[23.75]$^d$</td>
</tr>
<tr>
<td>c$^4$Σ$^{-}_u$</td>
<td>24.564</td>
<td>O$^+$($^4$S)+O(1D) [20.70] and O$^+$($^4$S)+O(3P) [18.73]</td>
</tr>
</tbody>
</table>

$^a$the vertical binding energy, adopted from Baltzer et al. [1992]

$^b$this is not totally correct, vibrational states v>3 lie above the predissociation limit of 18.73 eV, leading to O$^+$($^4$S)+O(3P) (e.g. Lafosse et al. [2001]). This contribution is neglected here due to a lack of further data for this process.

$^c$v=0...3, for higher vibrational states also O$^+$($^4$S)+O(1D) is possible but weakly populated (Lafosse et al. [2001]) ⇒ neglected here

$^d$the energy dependent branching ratio for the formation of $^2$D- and $^2$P-states is taken from Eland and Duerr [1998] and extrapolated.
6. Model developments during the thesis II: The ion chemistry model

eV) are assumed to lead to the formation of \( O^+(4S) \) (\(+\ O(3P) \text{ and } O(4D)\)), because \( B^2\Pi_g^- \) as well as \( b^4\Sigma_g^-(v>3) \) are lying in that energetic region would do so, though from energetic considerations also other products were possible.

For the non-dissociative ionisation it is differentiated between production of \( \text{O}_2^+ \) in ground state and in the \( a^4\Pi \) excited state.

**Photoionisation of \( \text{N}_2 \)**

The homopolar linear \( \text{N}_2 \) molecule absorbs significantly only below approximative 100 nm. At about 80 nm, ionisation sets in and for wavelengths smaller than 51 nm also dissociative photoionisations occur. Nicolas et al. [2003] have pointed out that dissociative photoionisations were investigated for many molecules but that \( \text{N}_2 \) is still not very well known. In the model’s wavelength region, the products are \( \text{N}_2^+ \) and \( \text{N}^+ + \text{N} \). The nitrogen atom can either be released in ground state (\( ^4S \)) or in the first excited electronic state (\( ^2D \)). The energy dependent ratio for non-dissociative/dissociative ionisations are taken from Rees [1999]. Nicolas et al. [2003] report that once the energy for the dissociation limit for formation of \( \text{N}(^2D) \) is reached, almost all neutral nitrogen atoms are of that kind, whereas \( \text{N}(^4S) \) is just formed to a significant extent in the narrow photon energy interval between 24.29 and 26.6 eV. This is adopted in the model.

**Photoionisation of \( \text{O} \)**

Photoionisation of atomic oxygen is only a minor ion source in the middle atmosphere, it is more important in the thermosphere. In the considered wavelength region, \( \text{O}^+ \) is almost exclusively produced in electrical ground state (\( ^4S \)), and as the doublets (\( ^2\Delta \)) and (\( ^2\Pi \)). The according wavelength dependent branching ratios are taken from Landold-Börnstein [2000].

![Figure 6.1: Photoionisation rates of \( \text{N}_2, \text{O}_2, \text{and atomic oxygen at latitude 30°N, on July 12th, calculated for a solar zenith angle of 30° during solar maximum.} \)](image)

**Photoionisation of \( \text{NO} \)**

The most important source of \( \text{NO} \) photoionisation in the upper atmosphere is Lyman \( \alpha \) radiation (\( L_\alpha \)). Due to a minimum in the \( \text{O}_2 \) absorption cross section in that wavelength region, \( L_\alpha \) can penetrate comparatively deep into the atmosphere. Absorption by other species is even much smaller than the one of \( \text{O}_2 \). A simple way of calculating the \( L_\alpha \) fluxes is therefore to account only for the extinctions by the total \( \text{O}_2 \) slant column above the point of interest (Brasseur and
6.1. Ionisation sources

Figure 6.2: Ionisation rates of NO due to Lyman $\alpha$ radiation, at latitude 30$^\circ$N, on July 12th, for different solar zenith angles during solar maximum, corresponding to figure 6.1. The left figure displays the situation for the hybrid model, the right one for the hybrid model with thermospheric NO.

This approach is similar to the one used in the SLIMCAT model to calculate photodissociation rates of O$_2$, H$_2$O, and CH$_4$ due to Lyman $\alpha$ radiation. Chabrillat and Kockarts [1997] point out that the O$_2$ absorption cross section for Lyman $\alpha$ is temperature dependent and that this influences the L$\alpha$ fluxes in the mesosphere. It was shown by Reddmann and Uhl [2003] that this temperature dependence in combination with the effect of resonant scattering changes the actinic flux in the mesosphere significantly. For high solar zenith angles, the contribution of L$\alpha$ scattered and emitted from the thermosphere, and especially from the geocorona becomes important. Quite sophisticated models are needed to account for these effects in detail, see for example Bishop [1999]. Such an approach seems by far too complex for being used in the model described here. On the other hand, it is known that the L$\alpha$ scattered from the geocorona is the most important source of ionisation under quiet night conditions and should be considered anyhow. The model uses the empirical approximations of Reddmann and Uhl [2003] to account for the temperature dependent O$_2$ absorption cross sections, and the parametrisations for scattered L$\alpha$, given by Thomas and Bowman [1986].

Figure 6.1 and figure 6.2 show the modelled photoionisation rates at mid latitude as a function of altitude during summer. While ionisation of O$_2$, N$_2$ and atomic oxygen is only relevant above the mesopause, photoionisation of nitric oxide occurs also at mesospheric levels. The comparison of NO ionisation rates from simulations with and without thermospheric NO (figure 6.2) indicates the importance of the thermospheric NO sources at higher altitudes, but their impact in the mesosphere is small.

Secondary ionisations by photoelectrons

The electrons released by photoionisations can have high kinetic energies, and cause further ionisations by collisions with atoms or molecules. They carry almost all of the surplus energy of the ionisation process, i.e. $\Delta E = E_{hv} - E_I - E_E$, where the three energies denote the photon’s energy, the ionisation energy, and excitation energy of the ion, respectively. For instance, the investigations of O$_2$ photoionisation by Lafosse et al. [2001] show that $\Delta E$ is almost entirely transferred to the photoelectron. The contribution of electron impact ionisation to the total ionisation of N$_2$ and O can be significant whereas it is of minor importance for O$_2$. It is considered in the model as follows:
All the photoelectrons are sorted according to their energies and stored in 1 eV wide energy intervals, ranging from 1 to 248 eV (this is the energy range which can be populated by the given setting of solar spectrum and considered species). Starting with the highest energetic bin, the number of electron impact ionisations of N\textsubscript{2}, O\textsubscript{2}, and atomic oxygen are calculated. The electrons are shifted downwards in the energy scheme according to their energy loss by ionisation and excitation, and the newly released electrons are added. This is repeated for all the other bins, cascading down the whole energy range, until all electrons are thermalised. Energy dependent cross sections for electron impact ionisation of N\textsubscript{2}, O\textsubscript{2}, and O are taken from Landold-Börnstein [2000], and [2003], respectively.

There are several other interactions of electrons with molecules, and atoms, as described in textbooks, e.g. Massey et al. [1969], and Massey [1969]. The most important processes which compete with ionisations are elastic momentum transfer, excitations of vibrational and rotational states, and electron attachment. These interactions are considered in the energy cascade scheme by the means of cross sections and energy loss values from Landold-Börnstein [2000, 2003].

An example of the resulting ionisation rates is shown in figure 6.3. A comparison with the photoionisation rates for the same conditions in figure 6.1 shows that the modelled electron impact ionisations of atomic oxygen exceed the effect of photoionisations, and for molecular nitrogen both ionisation processes yield comparable rates. However for O\textsubscript{2} the electron impact rates are much smaller than the photoionisation rates which dominate the photoionisations above the mesopause.

![Figure 6.3: Ionisation rates of N\textsubscript{2}, O\textsubscript{2}, and atomic oxygen due to impact of energetic photoelectrons at latitude 30\degree N, on July 12th, solar zenith angle of 30\degree during solar maximum, corresponding to figure 6.1.](image)

6.1.2 Galactic cosmic rays

Like energetic solar charged particles also corpuscular radiation of cosmic origin is able to cause atmospheric ionisations. The flux of such particles (mainly protons) into the Earth’s atmosphere is influenced by both the geomagnetic field as well as the Sun’s magnetic field. Along the solar cycle, the Sun’s magnetic structure varies, and this slightly modulates the penetration of cosmic charged particles into the atmosphere. Due to magnetic effects created by major solar flares, less particles enter in times of high solar activity than for quiet Sun conditions. This is the so-called Forbush effect. As a result of that, the ionisation intensity of cosmic radiation is somewhat
anticorrelated with the solar cycle. In the model, the ion productions due to cosmic rays are considered by parametrisations derived by Heaps [1978].

Figure 6.4 displays the total ionisation rates resulting from photoionisations, impact of secondary electrons, and GCRs. The galactic cosmic rays dominate the ionisation processes in the stratosphere, in the height region from approximative 60 to 82 km the L_α ionisation of NO sticks out, and above that photoionisation of O_2 is the governing process.

6.1.3 Energetic solar protons

In figure 6.5 the IPRs for a certain large SPE are depicted. A comparison with the ionisation rates for quiet ionospheric conditions shown in figure 6.4, reveals that the ionisation rates during such a large SPE exceed the other ionisations by orders of magnitude. Only in the thermosphere at small solar zenith angles, and below, say, 18 km, the background ionisation rates are larger than the calculated ionisation rates due to the precipitating protons. Therefore during major SPEs the middle atmospheric ion chemistry is governed by the forcings from the precipitating energetic particles. The ionisations products are mainly N_2^+, N^+, O_2^+, O^+ and atomic oxygen and nitrogen resulting from both direct proton impact as well as from impact of the energetic secondary electrons, e.g. Porter et al. [1976]. The production ratios for these species applied in the model are listed in table 6.7.
Figure 6.5: Daily averaged ionisation rates for some days during the solar proton event in July 2000, courtesy of Jörg Schröter.

Table 6.7: The initial production rates due to SPE impact in the model (IPR=total particle impact ionisation rate), unless noted otherwise the values are taken from Rusch et al. [1981].

<table>
<thead>
<tr>
<th>Species</th>
<th>Release rate</th>
<th>Branching</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>IPR</td>
<td>–</td>
</tr>
<tr>
<td>N$_2^+$</td>
<td>0.585 × IPR</td>
<td>–</td>
</tr>
<tr>
<td>N$^+$</td>
<td>0.185 × IPR</td>
<td>–</td>
</tr>
<tr>
<td>O$_2^+$</td>
<td>0.154 × IPR</td>
<td>32% O$_2^+$ (X$^2$) : 68% O$_2^+$ (a$^4$)$^a$</td>
</tr>
<tr>
<td>O$^+$</td>
<td>0.076 × IPR</td>
<td>40% O$^+$ (4S) : 40% O$^+$ (2D) : 20% O$^+$ (2P)$^b$</td>
</tr>
<tr>
<td>N</td>
<td>1.035 × IPR$^c$</td>
<td>42% N(4S) : 58% N(2D)</td>
</tr>
<tr>
<td>O</td>
<td>0.076 × IPR$^d$</td>
<td>100% (3P)</td>
</tr>
</tbody>
</table>

$^a$these are the electron impact branching ratios given by Rees [1999], neglecting higher excitations.
$^b$electron impact branching ratios [Rees, 1999].
$^c$this results from two processes: 1) proton impact: p$^+$ + N$_2$ → N$^+$ + N + e$^-$ + p$^*$ with 0.185 × IPR by which similar amounts of N(4S) and N(2D) are produced [Porter et al., 1976], and 2) dissociations by energetic secondary electrons: e$^+$ + N$_2$ → 2N + e$^*$ for which Zipf et al. [1980] give a N(4S)/N(2D) branching ratio of 40% to 60%. Rusch et al. [1981] state that the atomic nitrogen production rate from process 2 may be estimated to vary between 0.8 and 1.21 × IPR depending on the total ionisation and dissociation cross sections of N$_2$. They favour a low value to agree with the findings of Porter et al. [1976]. Consistently, Zipf et al. [1980] have found 0.8 × IPR. This value is adapted here.

$^d$the same value as for O$^+$ is assumed because e$^+$ + O$_2$ → O$^+$ + O + 2e is the major process for (direct) O$^+$ production, e.g. Rusch et al. [1981].
6.2 Anions

The negative molecular ion chemistry is established by the attachment of electrons to neutral species, and the atmospheric reactions which are believed to be most important in this respect are

\[ e + O_2 + M \rightarrow O_2^- + M \]
\[ e + O_3 \rightarrow O_2^- + O \]
\[ e + O_3 \rightarrow O_2 + O^- \]

The three body reaction is not effective in the rarefied air of the upper ionosphere, but for the D-region and lower E-region it governs the attachment of electrons to molecules. The second reaction is therefore often neglected. High resolution measurements have seemed to indicate that the electron attachment cross section for the last reaction peaks at low energies [Senn et al., 1999]. As these low energies are statistically strongly populated, this would have a considerable effect on the attachment rate. This is emphasised by Senn et al. [1999], and Mason [2003], but both publications miss to actually specify it in terms of numbers. A personal communication from Schreier [2006] has revealed that the large cross sections at low electron energies reported on by Senn et al., [1999] are at least partly due to a measurement artefact. Because of the remaining uncertainty, it has been assumed that there is no enhanced attachment rate for \( e + O_3 \rightarrow O_2 + O^- \). Electrons are removed from \( X^- \) by photodetachment, \( X^- + h\nu \rightarrow X + e \). This is simply accounted for by turning on a transformation of \( X^- \) to \( e \) under daylight conditions, which is comparable to the approach of Kazi [2002]. While all these processes do not change the total number of charged particles, recombinations of electrons and \( X^- \) with positive ions are sinks for ionic species in the model. The neutralisation and photodetachment reactions with rates are also listed in appendix A.1.

6.3 Numerical formulation

The model uses the SIS scheme, and the forward-Euler method for the slower reacting species, to integrate the ion chemical rate equations. In principle, the model can be used to simulate the whole time-evolution of the considered species online with the neutral chemistry of SLIMCAT. But due to the fact that some of the ionic reactions and interactions of ions with neutrals are very fast, this is very time consuming. Typically integration time steps as short as 1 ms are needed. For this study another mode of operation than the brute force fully integration has been chosen. Because of the high reaction rates, the ion chemical system tends to reach steady state rapidly after the external forcing in terms of ion production have changed, and this happens on much shorter time scales than the variations of the neutral chemistry calculated by SLIMCAT. Therefore the ion chemistry model does not have to be executed continuously. Instead, it can be called on demand, to calculate approximative steady state and the impacts on the neutral chemistry. This is, in short words, how it works:

The running ion chemistry model checks for “convergence” after every certain time interval, typically 10 s. Only if the relative changes of all charged species since the last check are smaller than a specified limit, the program stops, otherwise it continuous with integration. The limit can typically be set to 0.1%, smaller values do not change the results significantly but lengthen the execution times. The neutral species do not necessarily approach a limiting value within the ion chemistry scheme after a few seconds. For instance, atomic ground state nitrogen and
NO are usually produced linearly with time. The only reason for saturation could be significant consumptions of N\textsubscript{2} or O\textsubscript{2} which would require dramatically high ionisation rates. From their increasing concentrations in ionic steady state, the production rates of the neutrals can be determined, and then be used by SLIMCAT. Whenever the ion chemistry is executed, it is initialised with the uncharged species from the neutral chemistry. For the ions any arbitrary population can be used as long as the net charge is zero. A good initial guess can accelerate the convergence process significantly. Two choices are very useful: 1) The steady state results of a previous run can be used, this especially makes sense if the external parameters, such as SPE ionisation rates, and solar zenith angle, have not changed much. 2) From the total ionisation rate \( I \) and a mean recombination rate \( \alpha \), the total concentration of charged particles can be estimated:
\[
\sum_i [Y_i^+] = [e] + [X^-] = \sqrt{I/\alpha}.
\]
This can be distributed on the different species, according to their expected relative abundances, e.g. it is suitable to assign the positive concentrations mainly on O\textsuperscript{+}\textsubscript{2} and NO\textsuperscript{+}, and the negative charges on electrons in the upper model boxes and on X\textsuperscript{−} in the lower ones.

### 6.4 SPE production factors for NO\textsubscript{x}, HO\textsubscript{x} and O\textsubscript{x}

The ion chemistry model has been used to simulate the impacts of SPE ionisations in order to obtain production rates for the reactive neutrals of interest. The first finding was that the ionospheric background conditions influence the results in general only for SPE ionisation rates up to some hundred cm\textsuperscript{−3}s\textsuperscript{−1}. In the interesting IPR range from about \( 10^3 \) to \( 10^6 \) cm\textsuperscript{−3}s\textsuperscript{−1} the production factors for NO\textsubscript{x}, HO\textsubscript{x} and O\textsubscript{x} are basically independent from the other ionisation sources. Therefore it is indeed sufficient to solely consider the SPE IPRs.

In the ion chemistry scheme there is production of nitrous acid (HNO\textsubscript{2}) via
\[
\text{NO}^+ (\text{H}_2\text{O})_3 + \text{H}_2\text{O} \rightarrow \text{H}^+ (\text{H}_2\text{O})_3 + \text{HNO}_2.
\]

The very short lived HNO\textsubscript{2} molecule is not included in the SLIMCAT scheme and therefore it is considered by its primary reaction products. Some important gas-phase reactions of HNO\textsubscript{2} are given by Kituda et al. [1984]. Most of these reactions lead to a production of NO\textsubscript{x} and HO\textsubscript{x}. Additionally, for day-light conditions, there is rapid photodissociation, HNO\textsubscript{2} + h\nu \rightarrow \text{NO} + \text{OH}, e.g. Wall et al. [2006]. It is therefore assumed that each HNO\textsubscript{2} molecule immediately becomes NO + OH.

Figure 6.6 compares the NO\textsubscript{x} and HO\textsubscript{x} production rates from the ion chemistry model with the standard parametrisations given in section 3.2.5. In general there is slightly more production of HO\textsubscript{x} and NO\textsubscript{x} at higher altitudes than it is according to the standard parametrisation. The increasing NO\textsubscript{x} production with height is mainly due to the fact that the charge exchange reaction N\textsuperscript{2+} + O\textsubscript{2} \rightarrow N\textsubscript{2} + O\textsuperscript{2+} becomes less effective at higher altitudes which is not considered in the estimates of the standard production factors, see e.g. Rusch et al. [1981]. The partitioning of the NO\textsubscript{x} species is shown in figure 6.7, there tends to be more NO production per ion pair than it is with the standard parametrisation. While the NO\textsubscript{x} production does not significantly depend on ionisation rate, the HO\textsubscript{x} formation varies with IPR (figure 6.8). Finally, the production of O\textsubscript{x} species is shown in figure 6.9. The total O\textsubscript{x} output from ion chemistry is slightly smaller compared to the parametrisation. Interestingly, there is some direct production of ozone at higher altitudes, but this is by no means relevant for the total atmospheric ozone budget.
6.4. SPE production factors for NO$_x$, HO$_x$ and O$_x$

Figure 6.6: Production rates of NO$_x$ and HO$_x$ per SPE ion pair as a function of altitude calculated for a uniform ion pair production rate of $10^4$ cm$^{-3}$s$^{-1}$. The results from the ion chemistry model are shown by solid lines. The dashed lines belong to the standard parametrisation (section 3.2.5).

Figure 6.7: Production rates of nitrogen species per SPE ion pair as a function of altitude calculated for a uniform ion pair production rate of $10^4$ cm$^{-3}$s$^{-1}$. For comparison: The standard parametrisation assumes about 0.55 N(4S) and 0.7 NO per ion pair.
6. Model developments during the thesis II: The ion chemistry model

Figure 6.8: Production rates of HO$_x$ (including OH from HNO$_2$) per SPE ion pair as a function of altitude, calculated for different uniform IPRs.

Figure 6.9: Production rates of O$_x$ species per SPE ion pair as a function of altitude, calculated for a uniform IPR of $10^4$ cm$^-3$s$^{-1}$. For comparison: The standard parametrisation assumes 1.15 O$_x$ per ion pair.
7. The geomagnetic field scenarios

It was pointed out in section 2.2 that the regions in which energetic charged solar particles can enter the atmosphere depend on a variety of parameters. A proper consideration of all the intricate effects is quite challenging. Fortunately, it is not required to account for all of them within the scope of this work. Instead, a pragmatic approach can be used to describe the shielding properties of the geomagnetic field. For protons and He\(^{2+}\) in the SPE energy range, the areas of open field lines are appropriate approximations of the regions in which the particles penetrate into the atmosphere. It can further be assumed that the bulk of these particles directly passes through the magnetically open magnetosphere without being trapped (this does not apply for electrons which would be much more difficult to treat, but they are neglected anyway). Therefore the whole considered particle fluxes can be applied on the atmosphere in regions of open field lines while the rest of the globe is shielded.

In case of dipolar magnetic field configurations, the particle’s entering regions can be described by an energy independent cutoff latitude \(\lambda_c\) (i.e. the geomagnetic latitude which defines the edge of the magnetically open polar cusp regions). For the present-day magnetic field Jackman et al. [2000, 2005a] use a cutoff latitude of 60\(^\circ\) noting that actual values can differ from that depending on the spectrum of the solar protons. For the large SPE on August 1972 a value of 58\(^\circ\) for \(\lambda_c\) was determined by Reagan et al. [1981]. Such values correspond to a rather strong coupling between the solar wind and the magnetosphere [Siscoe and Chen, 1975] which are indeed not unrealistic during and right after large SPEs. More recently, Birch et al. [2005] have investigated variations in \(\lambda_c\) during three SPEs in the year 2001 exploiting proton counting rates from polar orbiting satellites. Their finding was that the cutoff latitude varies around 60\(^\circ\) and decreases by up to 10\(^\circ\) during the observed SPEs. They also report about small diurnal variation. Nevertheless, on average, \(\lambda_c=60\(^\circ\)\) seems to be a reasonable assumption for the current magnetic field. Therefore the present-day situation is represented by an energy independent \(\lambda_c=60\(^\circ\)\), and the geomagnetic axis tilted by 11\(^\circ\) with respect to the geographic axis. This setting will be labelled magnetic field scenario A in the following. It is displayed in figure 7.1. The regions which are open to particle precipitation in this scenario compare quite well with the simulations of Wentz et al. [2004]. Due to the tilt, the magnetic field’s topography translates into zonally averaged shielding factors for the two-dimensional atmospheric model. This shielding as a function of latitude is also indicated in figure 7.1.

Some other magnetic field configurations have been set up being characteristic for different realistic cases without claiming that they are real geo-historical ones. See table 7.8 for an overview of the scenarios. B (figure 7.2) stands for a very weak dipole field with the same tilt, ignoring any quadrupole or higher field parts. Its cutoff latitude corresponds to a dipole moment \(M\) of approximative 10% of the topical field strength if the scaling relation for dipolar magnetospheres \(\cos\lambda_c \propto M^{-1/6}\), [Siscoe and Chen, 1975] is applied. This approximative scaling can be used as long as the field is dominated by its dipole component though this simple approach
neglects the fact that the actual sizes of the magnetically open polar cusps depend on the field line merging efficiency which is again a function of the north-south component of the IMF, for details see Zieger et al. [2006]. Setting C (figure 7.3) is a dipolar configuration with cusps centred at the equator. Zieger et al. [2004] have investigated the case of such an equatorial dipolar magnetosphere by the means of MHD simulations. Their finding is that open field lines establish in the equatorial region most of the day. Due to the Earth’s rotation the openness of the magnetosphere varies along one day, and the field structure depends also on the IMF orientation. To simplify matters, a static cusp size of present value ($\lambda_c=60^\circ$) is assumed. This represents a snap-shot of a hypothetical reversal situation without any reduction of the magnetic field strength.

The scenarios D, E, and F originate from the investigations of non-dipolar magnetospheres by Vogt et al. [2007]. Pure quadrupolar fields give rise to a variety of magnetospheric configurations (due to different combinations of quadrupole field topology, and IMF orientation relative to the solar wind) Vogt et al. [2004] have investigated and classified quadrupolar magnetospheres. One special case, an axis-symmetric quadrupole field (with the quadrupole’s symmetry axis perpendicular to the solar wind flow) has been chosen to be scenario D. A pure axis-symmetric

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BASE</td>
<td>Completely shielded atmosphere, no SPEs</td>
</tr>
<tr>
<td>A</td>
<td>Present-day dipole-configuration, $\lambda_c=60^\circ$, $11^\circ$ tilt</td>
</tr>
<tr>
<td>B</td>
<td>Greatly reduced dipole, $\lambda_c=42^\circ$, $11^\circ$ tilt</td>
</tr>
<tr>
<td>C</td>
<td>Rotated dipole, equatorial polar cusp with $\lambda_c=60^\circ$</td>
</tr>
<tr>
<td>D</td>
<td>Pure quadrupole: Polar cusps $\lambda_c=60^\circ$ + equatorial belt of $\pm 10^\circ$ latitude</td>
</tr>
<tr>
<td>E</td>
<td>Dipole-quadrupole superposition, North: $\lambda_c=60^\circ$, and South: $\lambda_c=30^\circ$</td>
</tr>
<tr>
<td>F</td>
<td>Dipole-quadrupole superposition, North: $\lambda_c=30^\circ$, and South: $\lambda_c=60^\circ$</td>
</tr>
</tbody>
</table>
quadrupole field yields open field line regions around the poles and also in the equatorial zone. One particular north-south orientation of the IMF yields a polar cusp in one hemisphere and an additional equatorial band of open field lines, and the opposite IMF orientation opens the polar cusp in the other hemisphere. However, since the solar wind is highly variable these two principal configurations are combined to be scenario D. The cusps are chosen to have the same cut-off latitude as in case A, and the open field line region in the equatorial zone is assumed to cover a latitudinal range of $\pm 10^\circ$ (figure 7.4). Scenario E (figure 7.5) is a superposition of a dipole field with a quadrupole field. The quadrupole and the dipole contributions have the same magnetic field strength at the poles, and the dipole strength is approx. 10% of the present-day value. This configuration has two opposing magnetically open cusp regions in North and South of different sizes. It is a special case of field superpositions, for details see Vogt et al. [2006] (especially figure 4 and 5 therein). While in the northern region the field strengths add up, the cusp size in the South is much larger. This field scenario has been adjusted to have the same northern $\lambda_c$ as scenario A. The cut-off latitude in the South then has a dramatically lower value of $30^\circ$. Finally, the setting F is a similar dipole-quadrupole combination as E but with North and South switched.
Figure 7.4: Like figure 7.1 but here for the axis-symmetric quadrupole scenario D.

Figure 7.5: Like figure 7.1 but here for the dipole-quadrupole scenario E.
8. Single events

In this section the modelled impacts of some selected large SPEs are presented. Before different geomagnetic field configurations are considered, the event of July 2000 is used for some preexaminations, including comparisons of different model versions with satellite observations.

8.1 July 2000 - prelude

Signalised by smaller solar plasma ejections a few days in advance, a major solar X-ray flare with associated CME occurred on the 14th of July 2000 which gave rise to intense fluxes of energetic protons towards Earth, e.g. Bieber et al. [2002]. As July 14th is the anniversary day of the storming of the Bastille during the French Revolution in 1789, this SPE is also called the Bastille event. Between 14th and 17th of July 2000 the polar ionospheres were significantly disturbed (Liu et al. [2001], and Dmitriev et al. [2006]), and subsequent ozone losses during a few days after the event have been observed in polar regions and reproduced by the means of atmospheric modelling [Jackman et al., 2001].

In figure 8.1 the atmospheric ionisation impact due to energetic solar protons and He$^+$ around the mid of year 2000 is shown. Clearly the Bastille event can be identified, especially at lower heights to which only the highly energetic particles penetrate. At higher altitudes additional ionisations occur more irregularly due to lower energetic particles.

8.1.1 Models vs HALOE

Before the SPE’s chemical impacts on longer time scales are approached, simulation results are compared with measurements from the HALOE (Halogen Occultation Experiment) on board the UARS. During the Bastille SPE, HALOE provides data for latitudes around 66$^\circ$ North. Unfortunately, the measurement data only last until the 18th of July.

Simulations have been carried out with three different model versions, namely: 1) the family model, 2) the hybrid model, both applying the standard parametrisations for NO$_x$, HO$_x$ and O production (section 3.2.5), and 3) the hybrid model using parametrised production rates based on results from the ion chemistry model. A complete simulation of the ion chemistry would have been too time consuming. Anyhow, this model version hereafter will be referred to as the “hybrid ion model”. All three versions have the thermospheric NO sources included.

In order to compare the simulation results with the occultation measurements from HALOE, model outputs at solar zenith angles near 90$^\circ$ have been used. The longitudinal dependency of the satellite’s data is accounted for by 24 model runs performed with hourly shifted IPRs. From the 24 simulation results a weighted sum has been calculated. This approach is not fully consistent in terms of transport processes but the introduced errors should clearly be small during
such few days of model time.

Figure 8.2 compares the nitric oxide measurement data from HALOE with the simulation results. All models show significantly increasing NO mixing ratios after the SPE, being in good agreement with the HALOE observations. At the uppermost model altitudes, the simulations underestimate the abundance of nitric oxide before the 14th of July, but the values compare much better to the measurements than they would do without the thermospheric sources included. The reason for still having smaller NO mixing ratios at high altitudes than in the measurements is probably that the thermospheric NO injections into the model atmosphere correspond to rather quiet mean conditions of the year 1999 whereas in the time period considered here the solar activity was high.

Below the mesopause, all model versions tend to exceed the measured NO values. As the simulations also show higher NO mixing ratios than the measurements before the SPE sets in, it seems reasonable to consider rather the differences in nitric oxide than the absolute values to assess the SPE impact. For the model results, the NO differences are obtained by subtracting the values of base model runs for the same time period without SPE impact. For the HALOE data, the average of July 10th to July 13th is used as the reference. Figure 8.3 and figure 8.4 depict the nitric oxide mixing ratio differences. In general, the hybrid model causes the smallest NO increase. In the stratosphere the models basically coincide because there the hybrid model uses the family approach and the NO\textsubscript{x} production factors from the ion chemistry model and
Figure 8.2: Nitric oxide volume mixing ratios around the Bastille event in July 2000 as measured by the HALOE instrument at latitudes between 64° and 68° North in comparison with results of different model versions at 65.8° N. The HALOE data are daily averaged sunrise measurements inside the polar cusp, courtesy of Shahin Kazeminejad. The model plots show the sunrise averages of 24 simulations with hourly shifted ionisation rates.

from the standard parametrisation are almost the same. The hybrid ion model predicts more NO than the other versions at high altitudes which is due to the ion chemistry’s NO$_x$ production factors increasing with height. All models’ nitric oxide differences at high altitudes are smaller than the HALOE values before the 14th of July and larger afterwards. The first aspect could mean that the IPRs underestimate the impact of low energetic particles before the major event. It is also possible that thermospheric effects which are not simulated are responsible for these differences. The larger increase of the NO mixing ratios in the models after the Bastille event at high altitudes could also be attributed to the IPRs, thermospheric contributions or NO$_x$ production factors - it is not possible to make an assessment here based upon one measurement. Much more important for the purpose of this study is that the modelled NO differences compare quite well to the HALOE data at mesospheric levels, see e.g. the 70 km plot in figure 8.4. At lower altitudes the disagreement between simulations and measurements are again larger, but there the total NO production is significantly smaller.

The ozone mixing ratios for the same time period are shown in figure 8.5, and the differences at some selected altitudes in figure 8.6. While the modelled ozone differences at high altitudes do by no means match with the observations (see the plot for 85 km in figure 8.6), the results are much better in middle and lower mesosphere (70 km and 55 km plots). Similar to the situation for nitric oxide, the disagreement between modelled O$_3$ losses and observations are larger in the stratosphere than in the mesosphere. But again, the overall effect is smaller in the stratosphere. Furthermore, the stratospheric ozone differences calculated from the HALOE data show a pronounced trend already before the 14th of July. As this cannot be caused by the SPE, it has to
Figure 8.2: Differences of nitric oxide around the Bastille event in July 2000, corresponding to figure 8.2. The HALOE plot shows the NO mixing ratios relative to the mean value of July 10th to July 13th. For the models the differences to reference simulations without SPE impact are shown.

be attributed to the ordinary atmospheric variability.

For ozone depletion in catalytic cycles, the losses should in first approximation be proportional to the initial ozone concentrations. Therefore the relative ozone loss is the appropriate quantity by which the SPE impacts on ozone can be assessed. It is shown in figure 8.7. The family model seems to overestimate the stratospheric ozone losses on July 16th, July 17th, and 18th. The results of hybrid model and hybrid ion model are very similar. They also show higher ozone depletions in the stratosphere, but their values are closer to the HALOE observations than the ones of the family model.

Finally, figure 8.8 shows the differences between simulations and HALOE data for both NO differences and relative O$_3$ changes. While above approximative 75 km the hybrid model has the smallest differences to the measured NO, the hybrid ion model agrees the best with HALOE at lower altitudes. In terms of ozone, both the hybrid models yield very similar results. Their differences to the observed ozone losses are smaller than they are for the family model.

As such, the hybrid ion model is in better agreement with measurements in the relevant height regions than the other model versions are. Nevertheless, also the results from the family model agree fairly well with the observations. But it should be mentioned that the atmospheric situation which has been considered here is characterised by very short nights, basically polar summer conditions, under which the steady state approximation of the family model is more justified than at night. Therefore the different model versions should be compared at different latitudes as well, and also longer time scales have to be considered. This is done in the next section.
Figure 8.4: Differences of nitric oxide around the Bastille event at some selected altitudes. The HALOE data are relative to the mean NO values of July 10th to July 13th. For the models the differences to reference simulation without SPE impact are shown.

Figure 8.5: Ozone volume mixing ratios around the Bastille event in July 2000 as measured by the HALOE instrument at latitudes between 64° and 68° North in comparison with results of different model versions. The HALOE data are daily averaged sunrise measurements courtesy of Shahin Kazeminejad.
Figure 8.6: Ozone differences around the Bastille event at some selected altitudes.

Figure 8.7: Relative ozone losses, HALOE data in comparison with different model versions.
Figure 8.8: Absolute values of differences between model results and HALOE data. On the left the absolute differences of the NO differences are shown. The right plots display the absolute differences of the relative ozone changes.
8.1.2 Impacts on total ozone

The reduction of the total ozone column for all three model versions for the period until the end of year 2000 in the polar regions is depicted in figure 8.9 and figure 8.10. The differences are with respect to the undisturbed reference atmosphere BASE, and this applies to all differences shown in the following, unless noted otherwise. The responses to the SPE are very different in Antarctic and Arctic. July means polar summer conditions in the North with effective photochemical destruction of NO\(_x\) while in the South the reactive nitrogen radicals are longer lived which allows them to be transported down into the ozone layer. This mechanism is going to be considered in more detail in the next section, for the moment lets stick to the resulting total ozone losses to compare the different model versions. While the TOC reduction in the family model is larger than in the other models during the first days after the event (which corresponds to the finding in the previous section that the family model overestimates the effect on ozone directly after the SPE), it is smaller when the ozone loss has reached higher values about 80 days after the SPE. On average, the TOC reduction as a function of altitude looks similar for all three model versions (figure 8.11). As expected, the ozone losses are largest in the polar regions which are open to particle precipitation, and the impacts are most pronounced in the southern hemisphere because the Bastille event is a “south winter SPE”.

Though the three model versions yield the same qualitative picture, there are some differences between them. In the southern polar region, where the impact of the Bastille event is strongest, the total ozone losses of the family model differ from the results of the other models to a notable extent. In comparison with the hybrid ion model, the 6 month mean TOC reduction of the family model inside the polar cusp is by about 12% smaller.

![Figure 8.9](image)

Figure 8.9: Total ozone column changes due to the Bastille event till the end of year 2000 at 85.3° South, calculated with different model versions for the present geomagnetic field configuration.

8.1.3 Conclusion: Model selection

Because of its construction properties, the hybrid ion model should have an advantage over the other model versions. Though not totally exhaustive, the comparisons with the HALOE observations in section 8.1.1, have indicated that this model indeed gives a better picture of the short-term chemical SPE impacts than the other model versions. That these differences can
Figure 8.10: Total ozone column changes due to the Bastille event till the end of year 2000 at 85.3° North, calculated with different model versions for the present geomagnetic field configuration.

Figure 8.11: Average total ozone losses for the period of half a year after the Bastille event for the current geomagnetic field configuration as a function of latitude for different model versions.
build up notable effects on the TOC reduction was shown in the previous section. Therefore the hybrid ion model has been used for the investigations of the single SPEs presented in the following. Only for the simulation of the long time SPE series (section 9) the less time consuming family model has been chosen.

8.1.4 Model vs reality - a few words on errors

There are several error contributions to the modelling results. First of all, the model only accounts for a limited set of processes and reactions, and it does this on a finite two dimensional simulation grid. It has already been indicated in section 5 that the model’s zonally averaged transport approach leads to unrealistically large TOCs, especially at polar latitudes. As a consequence, the simulated TOC values are not very reliable, and the same applies to the SPE caused absolute ozone destructions. The latter are mainly due to catalytic reactions and therefore to a good approximation proportional to the stratospheric ozone content which again basically makes up the TOC. Thus, the modelled absolute ozone losses after a SPE are too large by about the same factor as the TOCs. By calculating the relative TOC differences, the factor of overestimation in principle cancels out. Because of that, the SPE impacts on the total ozone column are going to be expressed mainly in terms of relative O$_3$ differences in the following.

The most critical input parameter for the simulations of the SPE effects are the ion pair production rates. At the same time these values, as well as the production rates for reactive neutrals, are afflicted with some uncertainties (section 3.2.5). An error of $\pm 10\%$ seems realistic. In order to get an impression of the IPR error impacts on the model results, additional simulations of the Bastille event have been carried out with modified IPRs. Figure 8.12 shows the resulting TOC reductions for the Bastille event with IPRs modified by $\pm 10\%$. In the southern polar region the resulting effect on the one year relative TOC change is about +20% and -13%, respectively.

![Figure 8.12: The one year mean total ozone column differences after the Bastille event for the original ion pair production rates, and for rates changed by $\pm 10\%$.](image)
The chemical scheme of SLIMCAT consists of more than one hundred reactions. The associated reaction coefficients originate from measurements and they introduce uncertainties in the simulations. Due to temperature dependencies, the reaction rates are also influenced by the meteorology code. It is basically impracticable to account for the error contributions from all the model’s reactions. In order to make at least an assessment of the main photochemical uncertainties with respect to SPE impacts, some important reactions have been selected to be looked at. They are listed in table 8.9. For each of them the reaction rate coefficient was varied independently by ±1% and then simulations with and without SPE have been performed. For each modified reaction, the atmosphere was modelled starting ten years before the SPE to avoid any effects of abrupt changes, and to ensure that there was enough time for all remote atmospheric impacts to happen. For some of the reactions the effects on TOC is large, but this then applies for both the reference atmosphere as well as for the atmosphere experiencing the SPE, and the resulting impacts on the relative TOC reduction are not that dramatic, see table 8.9. Assuming that the errors are uncorrelated, and that each reaction changes the TOC reduction in a linear manner, the resulting error is about 7%.

Photochemical and IPR error together (uncorrelated) are then approximative 18%. Finally, if the difference of the SPE caused TOC reduction of family and hybrid ion model (section 8.1.2) is regarded as an additional independent error of the family model, its resulting total error is about 22%. These numbers are rough estimates, their numerical values should not be taken too seriously, and rather be regarded as orders of uncertainty of the model results.

Table 8.9: The reactions of which the rate coefficients have been varied by ±1%, and their averaged (±) impacts on the mean relative TOC reduction during one year after the Bastille SPE.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Impact [%] on ΔTOC [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>O + O₂ + M → O₃ + M</td>
<td>2.8</td>
</tr>
<tr>
<td>O + O₃ → 2 O₂</td>
<td>2.6</td>
</tr>
<tr>
<td>NO₂ + O → NO + O₂</td>
<td>2</td>
</tr>
<tr>
<td>NO + O₃ → NO₂ + O₂</td>
<td>2</td>
</tr>
<tr>
<td>O₃ + hν → O₂ + O</td>
<td>4.5</td>
</tr>
<tr>
<td>O₂ + hν → 2 O</td>
<td>3.5</td>
</tr>
<tr>
<td>NO + hν → N + O</td>
<td>1</td>
</tr>
<tr>
<td>NO₂ + hν → NO + O</td>
<td>1.6</td>
</tr>
</tbody>
</table>

8.1.5 The Bastille SPE shifted to January

The modelled ozone losses due to the Bastille event are largest in the southern polar region because there the particle impact coincides with winter conditions. What if the same event would have occurred half a year later? The answer is given by figure 8.13. As expected, the ozone destruction increases in the northern polar region, but the ozone loss peak is narrower than for the original Bastille event in the southern polar region, and it occurs with some delay. This is due to unequal atmospheric transport conditions. The strength and the seasonal characteristics of the meridional circulation differ in both hemispheres. Additionally, the polar vortex is stronger in the southern polar region than in the Arctic which inhibits the ozone influx from lower latitudes more drastically and ozone needs more time to recover after the SPE. The simulations
show that the mean ozone losses during half a year after the SPE is larger in the South than it is for the shifted SPE in the North, but on a two year basis the differences basically have levelled out, see figure 8.14.

Averaging the ozone losses along a fixed time interval after the event seems not to be the best way of assessing the SPE’s impact on ozone, especially not with respect to hemispheric differences, because the TOC reduction is not largest directly after the event but with some weeks of delay, and this delay varies with latitude. A more suitable measure considers the mean ozone difference within a time interval of fixed length starting a certain time after the event. For a specific offset of the time window, the mean ozone difference is largest. This value will be called maximum mean ozone difference. As the offset of the time interval is different for different latitudes, the maximum mean ozone difference as a function of latitude does not give a simultaneous picture, it is instead a collection of the maximum mean values for the different latitudes. Figure 8.15 shows the maximum mean TOC differences for a period of one year. They look very similar for the original Bastille event and for the shifted SPE.

From these results of this single SPE no general conclusion can be drawn on the hemispheric differences of atmospheric responses to solar proton events. The long time series of SPEs being addressed in section 9 will provide the appropriate basis to study this issue.

8.2 July 2000 - geomagnetic field variations

The long term ozone depletion due to a SPE depends on the transport of the reactive NO\textsubscript{x} species into the ozone layer. Therefore it is helpful to start with a consideration of the reactive nitrogen compounds. In terms of transport it is useful to consider the odd nitrogen NO\textsubscript{y}=NO\textsubscript{x}+NO\textsubscript{3}+HNO\textsubscript{3}+HO\textsubscript{2}NO\textsubscript{2}+ClONO\textsubscript{2}+2\times N\textsubscript{2}O\textsubscript{5} instead of NO\textsubscript{x} because it contains basically all (potentially) reactive nitrogen species. Figure 8.16 shows the resulting increase of NO\textsubscript{y} after the Bastille event for the current geomagnetic field scenario A in the polar regions which are open to particle precipitation. In both hemispheres the initial NO\textsubscript{x} production due to the SPE is the same, but the photochemical fates of the nitrogen compounds differ significantly.
Figure 8.14: Total ozone column changes after the Bastille event and for the same event shifted by 182 days.

Figure 8.15: Maximum 12 month total ozone column changes after the Bastille event and for the same event shifted by 182 days in the left figure. For the sake of comparability the shifted SPE is displayed with North and South switched in the right figure.
under summer and winter conditions. The NO\textsubscript{y} enriched air is efficiently transported downwards in the Antarctic winter, and the NO\textsubscript{y} decay is slower than under the polar summer conditions in the other hemisphere.

The axis-symmetric quadrupole scenario D has open field lines at the equator. The resulting NO\textsubscript{y} signal of the Bastille SPE for this scenario is displayed in figure 8.17. In contrast to the particle impact in the southern polar region, there is almost no downward transport of NO\textsubscript{y} into the tropical stratosphere. At mesospheric heights, the increased NO\textsubscript{y} concentrations are photochemically removed quite rapidly, and only in the upper stratosphere NO\textsubscript{y} remains on significantly enhanced levels for some weeks.

For comparison, the HO\textsubscript{x} increase in the southern polar region due to the Bastille SPE is depicted in figure 8.18. The HO\textsubscript{x} species released by the SPE are rather short-lived. The direct impact on the HO\textsubscript{x} chemistry is significant only during a few days after the ionisations have occurred. Therefore HO\textsubscript{x} causes some immediate ozone destruction but does not affect the ozone chemistry on longer time scales. Because of this, in the following the focus is on NO\textsubscript{y}.

In figure 8.19 it is displayed how the increased abundance of NO\textsubscript{y} evolves for the different field configurations. In general, the total NO\textsubscript{y} increase is largest in the southern polar region. For scenario D and, less pronounced, for C, there is a NO\textsubscript{y} peak during and shortly after the SPE at low latitudes from where some NO\textsubscript{y} is transported towards the southern polar region, but the NO\textsubscript{y} lifetimes are drastically shorter at low latitudes and therefore this effect is not very strong. Due to the largest Antarctic cusp size, the quadrupole-dipole scenario E has the highest increase of total NO\textsubscript{y}, followed by the reduced dipole B and the other dipole-quadrupole D.

The differences between the present day situation and E in the North, and F in the South arise from the missing tilt of geomagnetic axis with respect to the geographical one (the cusp sizes are the same). For these scenarios the NO\textsubscript{y} increase is larger than it is for the current configuration. The differences in NO\textsubscript{y} correspond to distinct impacts on ozone, see figure 8.20 and figure 8.21. In general the effect on ozone is much stronger in case of precipitating particles in the polar regions than it is at lower latitudes. For the geomagnetic field scenarios with open field lines in the geographical polar regions, the ozone losses increase with cusp size, and they are more pronounced for the scenarios with geomagnetic field axis aligned to the geographical axis compared to the scenarios with tilt.

There is some stratospheric ozone loss in the Arctic for the equatorial dipole, see figure 8.20, after the NO\textsubscript{y} enriched air from the tropics has reached the polar region. But it is much smaller than for the other cases, including the present day configuration.

Locally, there is some moderate ozone gain which is mainly due to two effects, namely 1) the so-called ozone self healing which is caused by increased UV fluxes below a region of ozone losses which in turn lead to higher O\textsubscript{3} production rates, and 2) the increasing NO\textsubscript{y} concentrations after the SPE facilitate the formation of reservoir species such as ClONO\textsubscript{2} and BrONO\textsubscript{2}. For both aspects see Jackman et al. [2000] and references therein. As the model represents an atmosphere with the high stratospheric halogen load of year 2000, the formation of ClONO\textsubscript{2} and BrONO\textsubscript{2} is a relevant process which transfers ozone depleting halogen substances into inactive ones. The issue of different atmospheric conditions will be considered in the section of the Carrington-Hodgson SPE of 1859 later in the manuscript (section 8.5).

Figure 8.22 depicts the modelled ozone differences during the SPE on July 14th which basically coincide with the ionisation patterns through particle impact. There are some hemispheric differences even for the scenarios with North-South symmetric field configurations. As the ion pair production rates in the mesosphere and upper stratosphere have raised by orders of magnitude only a few hours ago, transport processes are of minor importance, and the differences are mainly due to photochemical reasons. Most striking is the low SPE caused ozone destruction in the
Figure 8.16: Modelled NO\textsubscript{y} difference after the Bastille event in the polar regions for scenario A, in the upper figure for South, and in the lower one for North.

Figure 8.17: Modelled NO\textsubscript{y} difference after the Bastille event in the equatorial regions for scenario D, corresponding to figure 8.16.
Antarctic stratosphere. This is due to the small concentrations of atomic oxygen under polar night conditions. Atomic oxygen is required to keep the catalytic NO/NO$_2$ cycle going:

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O} \rightarrow \text{NO} + \text{O}_2
\]

During daylight conditions, there is also photolysis of nitrogen dioxide, $\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$. At night, $\text{NO}_2$ is instead removed through $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$. This, together with $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$, destroys some ozone, but the effect is small compared to the catalytic depletion in the presence of atomic oxygen. There is indeed a release of atomic oxygen during the SPE by

\[
\text{N}(^2\text{D}) + \text{O}_2 \rightarrow \text{NO} + \text{O} \\
\text{NO} + \text{N}(^4\text{S}) \rightarrow \text{N}_2 + \text{O}
\]

which even exceeds the net formation of NO because of the close production rates for $\text{N}(^4\text{S})$ and $\text{N}(^2\text{D})$, but the atomic oxygen is rapidly converted to ozone via $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$. At higher altitudes, this three body reaction is less effective, and also the HO$_x$ chemistry dominates the impacts on ozone. Through $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2 \text{O}_2$ hydroxyl can be recycled from HO$_2$ without atomic oxygen needed. Together with $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$ this provides a catalytic destruction cycle. Therefore there is ozone depletion in the upper part of the middle atmosphere during polar night. In regions with solar insulation the mesospheric ozone losses are smaller, and there tend to be a local minimum around 70 km which is a result of ozone self healing.

Figure 8.23 shows the ozone differences one month later. The regions of the main ozone losses have propagated downwards, and are centred around 35 to 40 km. Especially the equatorial dipole case C shows an interesting O$_3$ loss distribution: Though the particle impact was restricted to tropical latitudes, the largest ozone loss is found in the sub-polar and polar South. This is due to the NO$_y$ transport mentioned above. Right in the polar night region, especially above the stratopause, there is some ozone gain, but with maximum values of some tens of ppb it is not very important for the total ozone.

The SPE’s impact on the Antarctic TOC for all geomagnetic scenarios is shown in the figures 8.24, and 8.25. Only for the rotated dipole the ozone losses are smaller than for the present
Figure 8.19: The modelled increase of the total atmospheric NO\textsubscript{y} column as a function of time and latitude during 2.5 years after the Bastille event for all geomagnetic field scenarios.
day field configuration. For all other cases the SPE impacts are larger, and for some of them, like the reduced dipole and scenario E, there is substantially more ozone destruction. At the equator (figure 8.26) the resulting TOC reductions are significantly smaller. The total ozone losses of all scenarios as a function of latitude and time are given in figure 8.27, and the maximum mean ozone differences for one year in figure 8.28. Except for the equatorial dipole, the ozone losses are larger for all scenarios than for the present day field configuration. Alternatively, the present day geomagnetic field situation can be regarded as the reference to which the other scenarios are compared because the current setting has basically been stable for about 780 thousand years and can be thought of as some kind of base configuration. The differences of the relative TOC changes shown in figure 8.29 indicate that in case of the equatorial dipole the polar and sub-polar ozone destruction is significantly smaller than for scenario A. At the same time the additional ozone losses in the tropics are not very pronounced, though the size of the regions open to particle precipitation equals the one of scenario A. Even for scenario D with its magnetically open equatorial band, the total ozone losses at low latitudes do not exceed 0.2%. Of the same order is the difference of TOC reduction for scenario F. Its larger cusp size in the North is not very relevant for the July 14th event. Significantly larger are the additional ozone losses for scenario B, and, even more, for E with their enlarged cusp sizes in the southern polar region.

8.2.1 Impacts on UV-B

The ozone losses give rise to enhanced fluxes of shortwave radiation at the Earth’s surface. The actual effect strongly depends on the particular wavelength region. Due to ozone’s strong absorption in the Hartley band, the radiation in the UV-B regime (280–315 nm) is very sensitive to ozone changes. Though there are some uncertainties concerning the detailed harmfulness of ultraviolet radiation of different wavelengths, it is clear that exposure to UV radiation can cause several acute and chronic health effects on the skin, on the eyes, and on the immune system. Two of the most dramatic effects are increasing risks of skin cancer and cataracts. Often, the erythemal weighted UV-B radiation is used to quantify the flux of shortwave radiation by a single number. Its relative change can simply be estimated from the relative change in the total ozone column by

$$\frac{\Delta F}{F} = -\left(\frac{\Delta \text{TOC}}{\text{TOC}}\right) \times AF$$

where F denote the flux of erythemal weighted UV-B radiation, and AF the radiation amplification factor [WMO, 1999]. The AF is not constant but varies due to scattering with the solar zenith angle and depends also on the actual ozone profile. Here a mean AF of 1.1 has been used. Later, in section 9.2, results from radiative transfer simulations will show that this value is indeed a good approximation. Figure 8.30 presents the changes of the erythemal weighted UV-B radiation for all scenarios. Especially for the scenarios B and E the values increase in the southern polar region for several month by one to more than four %.
8.2. July 2000 - geomagnetic field variations

Figure 8.20: Modelled ozone difference after the Bastille event in the southern polar region for all scenarios.

Figure 8.21: Modelled ozone difference after the Bastille event for scenario D at the equator.
Figure 8.22: The modelled ozone differences at noon on July 14th for all magnetic field scenarios.
Figure 8.23: The modelled ozone differences on August 14th, one month after the Bastille event, for all magnetic field scenarios.
Figure 8.24: Total ozone column changes from mid of year 2000 to mid of year 2001 in the southern polar region for the scenarios A, B, and C.

Figure 8.25: Total ozone column changes from mid of year 2000 to mid of year 2001 in the southern polar region for the scenarios D, E, and F.

Figure 8.26: Total ozone column changes from mid of year 2000 to mid of year 2001 at the equator for the scenarios A, C, and F.
Figure 8.27: Modelled reduction of the total ozone column due to the Bastille event for all field scenarios.

Figure 8.28: Maximum 12 month mean total ozone losses after the Bastille event as a function of latitude for the different magnetic field scenarios.
Figure 8.29: Absolute differences of the maximum 12 month mean relative TOC differences with respect to the current geomagnetic field configuration.

Figure 8.30: Modelled increase of the erythemal weighted UV-B radiation due to the Bastille event for all field scenarios.
8.2. July 2000 - geomagnetic field variations

8.2.2 Impacts on atmospheric temperature

Due to its shortwave absorptions, ozone is an important heat source in the stratosphere. Additionally, emissions in the 9.6 $\mu$m ozone band contribute to radiative cooling, and absorption in that wavelength region can also cause some heating. The net longwave effect depends on the actual temperature profile, the abundance of other absorbers and emitters, and is therefore a function of height, see for instance Peixoto and Oort [1992]. Thus, the SPE caused ozone losses discussed in the previous sections might alter the atmospheric temperatures. But there is not only an ozone loss compared to the BASE atmosphere, at the same time the abundance of nitrogen dioxide, which is an important shortwave absorber as well, is increased. The additional heating by NO$_2$ absorption partly compensates the effect of reduced ozone absorption.

Figure 8.31 shows the temperature changes one month after the Bastille event, and contrasts them with the ozone losses. In the northern polar stratosphere there is generally a temperature decrease, except for scenario C which does not have any significant ozone destruction there. Below approximative 35 km there is no significant temperature decrease though there the peak of ozone destruction is located. This can in the first instance be understood by the fact that the decreasing ozone column above 35 km leads to more downwelling shortwave radiation which in turn causes more heating at lower altitudes. But the temperature changes cannot solely be explained by locally altered heating and cooling. The changed diabatic heating rates influence the atmospheric circulation which again causes remote temperature differences due to changed adiabatic heating or cooling, and the changed transport of radiative active substances also feeds back on the heating rates, and so on. In the southern polar night region the heating through UV absorption does not play a role. The temperature changes seen there are due to differences in longwave heating and cooling and altered adiabatic heating rates. The figure 8.31 is a snap-shot of temperature changes. In section 9 long term mean values will be presented.
Figure 8.31: The modelled temperature differences on August 14th for all magnetic field scenarios. Positive values correspond to higher temperatures compared to the atmosphere without SPE impact. Contour lines indicate the corresponding ozone losses.
8.3 October/November 2003

Late October 2003, at the end of solar cycle 23, three large sunspot groups emerged, e.g. Delfs [2004], which gave rise to a series of large flares which persisted into November. After October 22nd, several CMEs occurred [Skoug et al., 2004], and on November 4th an intense X-ray flare, the strongest since measurements began in the 1960s, has been detected at the edge of the solar disc before the active region left for the Sun’s back side and the Earth-directed particle output decreased significantly. Especially in the period 28–31 of October the energetic solar proton fluxes were substantially increased. The atmospheric ionisation impact of the energetic solar protons and He$_2^+$ for October/November 2003 is depicted in figure 8.32, and figure 8.33. The ionisation signature is broader than the one of the July 14th SPE.

While the previously discussed Bastille event coincided with winter in the southern hemisphere, the October/November 2003 SPE occurred after autumnal equinox and thus caused stronger effects in the northern hemisphere. NO$_y$ concentrations remain on high levels especially in the North for all scenarios for several month (figure 8.34) and consequently the total ozone losses are strongest in the northern hemisphere (figure 8.35). The larger the Arctic cusps size the larger the ozone losses. The latitudinal dependency of TOC reduction for the different scenarios is depicted in figure 8.36, and with respect to the present day configuration in figure 8.37. In terms of NO$_y$ formation and subsequent O$_3$ depletion the October/November SPE is slightly larger than the Bastille event.

So far the results were for the October/November 2003 SPE applied to the initially undisturbed atmosphere. Especially for the scenarios with large areas open to particle precipitation, the Bastille SPE influences the atmospheric conditions for several month up to years. From that the question arises whether there could be any significant aftereffect of the July 14th event on the atmospheric responses to the October/November SPE more than three years later. This has been investigated by additional simulations of the October/November SPE applied to the atmospheres which had experienced the Bastille event before. With the previous July 2000 SPE considered, the impacts of the second event are indeed somewhat larger. There is an accumulation of NO$_y$ (compare figure 8.38 with the corresponding plots in figure 8.34), and the resulting ozone losses are larger. Figure 8.39 displays the TOC reduction in the northern polar region. In figure 8.40 the effect on the ozone destruction as a function of latitude is shown. For the scenarios B and E with their large magnetic cusps in the South, the Bastille SPE continues to have a noticeable effect in the southern hemisphere. In case of the equatorial dipole C there is a significant increase of TOC losses in the northern polar region, though still being smaller than for the other scenarios. This shows that large events can indeed have impacts on time scales of several years, and that they might influence subsequent SPEs. It should be mentioned that between the considered two major SPEs several other events have occurred of which some have caused substantial NO$_y$ production as well [Jackman et al., 2005b]. Therefore the possible interference between SPEs should even be larger than the simulations have shown here.
Figure 8.32: Hourly averaged ion pair production rates at some selected altitudes from beginning of October to late November 2003, courtesy of Friedhelm Steinhilber. Day 301 corresponds to October 28th. These data have been calculated by the Monte Carlo method using proton and He\textsuperscript{2+} fluxes from GOES.

Figure 8.33: Daily averaged ionisation rates for some days during the solar proton event(s) in October/November 2003, courtesy of Jörg Schröter.
Figure 8.34: The modelled increase of the total atmospheric NO\textsubscript{y} column as a function of time and latitude during about 3 years after the October/November 2003 event for all geomagnetic field scenarios.
Figure 8.35: Modelled reduction of the total ozone column due to the October/November 2003 event for all field scenarios.

Figure 8.36: Maximum one year mean relative ozone losses due to the October/November 2003 SPE as a function of latitude for the different magnetic field scenarios.
Figure 8.37: Differences of the maximum one year mean relative ozone differences due to the October/November 2003 SPE with respect to the current geomagnetic field configuration.

Figure 8.38: The modelled increase of the total atmospheric NO\textsubscript{y} column as a function of time and latitude during about 3 years after the October/November 2003 event for two characteristic magnetic field scenarios if the previous Bastille event is considered.

Figure 8.39: Total ozone column changes after the October/November 2003 SPE in the northern polar region for scenario F. Shown are the response in an atmosphere which experienced the Bastille event before, and in an atmosphere without previous SPE disturbance.
Figure 8.40: Maximum one year mean relative ozone differences due to the October/November 2003 SPE. Solid lines show the situation if the previous Bastille event is considered, the crosses if not.
8.4 October 1989

There had been a sequence of four major SPEs which gave rise to significantly increasing fluxes of energetic particle towards Earth during 19th to 27th of October 1989. In terms of atmospheric impacts this was the largest SPE series which has been detected ever since direct measurements started more than four solar cycles ago. It caused almost twice as much middle atmospheric NO\textsubscript{y} production than the Bastille event or the October/November 2003 SPE [Jackman et al., 2005b]. The used IPRs for the simulation of the October 1989 SPE are daily averages originating from Bethe Bloch calculations, see figure 8.41 for ionisation profiles at some selected days. In contrast to the IPRs for the previously considered SPEs, for this event only protons have been taken into account, and therefore in comparison they should be somewhat smaller (of the order of 10%).

As displayed in figure 8.42, the qualitative patterns of NO\textsubscript{y} column increase are similar to the SPE of October/November 2003. This does not surprise because both October events coincided with very similar atmospheric conditions. The NO\textsubscript{y} production due to the SPE of October 1989 is significantly higher than the one of the previously considered SPEs. As a result, also the ozone losses are larger, see figure 8.43. Due to its large cusps size in the North, scenario F yields the highest impacts on total ozone in the northern polar region, exceeding 2\% for more than one year after the SPE. Scenario E again has the highest total ozone destruction in the southern polar region. Maximum mean TOC reductions are shown in figure 8.44 and figure 8.45. As expected, again the scenarios with large cusps in polar regions cause the largest effects while the impacts for the equatorial dipole are significantly smaller. Consequently, the UV fluxes increase especially at high northern latitudes, figure 8.46.

Figure 8.41: Daily averaged ionisation rates for some days during the solar proton event(s) in October 1989, courtesy of Jörg Schröter.
Figure 8.42: The modelled increase of the total atmospheric NO\(_y\) column as a function of time and latitude during about 3 years after the SPE of October 1989 for all geomagnetic field scenarios.
Figure 8.43: Modelled reduction of the total ozone column due to the October 1989 SPE for all field scenarios.

Figure 8.44: Maximum mean relative total ozone losses after the October 1989 SPE as a function of latitude for the different magnetic field scenarios.
Figure 8.45: Differences of the maximum mean relative ozone losses with respect to the current geomagnetic field configuration.

Figure 8.46: Modelled increase of the erythemal weighted UV-B radiation due to the October 1989 SPE for all field scenarios.
The white light flare and the associated magnetic storm of September 1st, 1895 had not just been the first space weather event recognised, it is also believed to be one of the largest solar events since then. As it had been observed by Carrington and Hodgson (section 2.1) it is going to be called Carrington-Hodgson Event (CHE) in the following. Cliver and Svalgaard [2005] have compared the largeness of that SPE with other major solar events in different categories such as X-ray activity, energetic solar proton fluences, Sun-Earth transit time and others. In each of these categories they found close peers or superiors, but in terms of proton fluences, which are most important for the atmospheric impacts, the CHE has been the largest event within the last 150 years.

There are, of course, no direct measurements of the CHE's particle fluxes, but the event has left its mark in nitrate deposits in firn and ice cores in both polar regions. McCracken et al. [2001a+b] have analysed such proxy data and found more than 150 impulsive nitrate events in Greenland ice core between 1561 and 1994 which they have related to major solar events. The notion is that NO\textsubscript{y} released by SPEs is a progenitor of nitrate in polar firn and ice, though there are some issues regarding the necessary transport of NO\textsubscript{y} down into the troposphere. McCracken et al. [2001a] argue that the downward transport in polar regions could be facilitated by sedimentation of large ice particles which possibly act as carriers for nitric acid. Events such as the CHE correspond to impulses in the nitrate concentrations from which the fluences of protons with energies >30 MeV can be estimated [McCracken et al., 2001a]. Additional assumptions have to be made in order to yield the energy dependent proton fluxes which are required to calculate the atmospheric ionisation profiles. For this purpose the energy spectrum of the major SPE in August 1972 has been used to scale the CHE with. The SPE of 1972 was chosen because it is the largest single event of which the particle fluxes have been measured by satellites and is believed to be a typical representation of a large event, for details on the scaling process see Steinhilber [2005]. From the resulting energy spectrum the ionisation rates have been calculated by the means of the Bethe Bloch method, the resulting ionisation profile is shown in figure 8.47.

![Figure 8.47: Daily averaged ionisation rate for the solar proton event on September 1st, 1895, courtesy of Jörg Schröter.](image)
In order to be comparable with the previous SPEs, the CHE has been applied on the model atmosphere of year 2000. The resulting NO$_y$ increases are large. In the North they are quite similar to the results for the October 1989 SPE, and in the South they exceed even the values of the Bastille event which occurred in southern winter. Figure 8.49 shows the resulting TOC reductions as a function of latitude and time. They are the largest presented in this manuscript so far. The figures 8.50 and 8.51 display the maximum mean differences, and the estimated differences of erythemal weighted UV-B radiation in figure 8.52.

Additionally, the CHE has been studied in an atmosphere without anthropogenic halogen compounds to get an impression of the role these ozone depleting substances play. The total halogen load of the pre-ozone hole atmosphere is not know in very great detail, though for the chlorofluorocarbons (CFCs) and halons the situation is clear as they have artificial sources only. See appendix A.2 for the halogen concentrations as they have been used to model the atmosphere prior to the increasing halogen load during the industrial age.

Figure 8.53 compares the total ozone columns in both atmospheres in the southern polar region after the CHE and the TOCs without SPE impact, and in figure 8.54 the differences in both atmospheres are shown. Though the absolute TOC values should not be taken too seriously (because they are too large, section 5, they still can provide an insight in the basic differences of the atmospheric scenarios. The SPE caused ozone losses are larger in case of the atmosphere with low halogen load, simply because there is more O$_3$ that can be depleted and because the formation of the reservoir species CIONO$_2$ and BrONO$_2$ is less pronounced. Interesting are the periods of ozone hole conditions in the industrial atmosphere in spring times. The first ozone hole forms directly after the SPE (it extends between approx. 10 to 110 days after the CHE), and its effect on the total ozone is much larger than the SPE impact. Especially at the beginning of the ozone hole situation, interference of the activated halogen substances with the enhanced abundance of reactive nitrogen compounds leads to smaller O$_3$ losses than in the atmosphere with low halogen load. Afterwards there is some TOC reduction without great variations caused by the SPE, and one year later, when the next ozone hole occurs (around day 380 after the CHE), larger ozone losses are observed for the present-day atmosphere than during the first ozone hole. This indicates the interferences of halogen and nitrogen chemistry and their disturbances by anthropogenic substances and SPEs, respectively. Additionally, the comparison of the SPE impacts on ozone with the TOC reduction due to anthropogenic substances reveals that the latter cause more dramatic effects. This even holds for such an outstanding SPE as the CHE in combination with the extreme magnetic field scenario E. Nevertheless, in this case the SPE impacts on the TOC are yet considerable, and they gain importance by the fact that they are long lasting. In contrast to ozone hole situations, the SPE impacts persist long into the polar summer because the photochemical lifetime of NO$_y$ is long enough in mid and lower stratosphere.
Figure 8.48: The modelled increase of the total atmospheric NO$_x$ column as a function of time and latitude during about 3 years after the September 1st white light flare if it is applied in the year 2000.
Figure 8.49: Modelled reduction of the total ozone column due to the Carrington-Hodgson SPE in year 2000 for all field scenarios.

Figure 8.50: Maximum mean relative total ozone losses after the Carrington-Hodgson SPE in year 2000 as a function of latitude for the different magnetic field scenarios.
Figure 8.51: Differences of the maximum mean relative total ozone losses after the Carrington-Hodgson SPE in year 2000 as a function of latitude for the different magnetic field scenarios.

Figure 8.52: Modelled increase of the erythemal weighted UV-B radiation due to the Carrington-Hodgson SPE in year 2000 for all field scenarios.
Figure 8.53: Antarctic total ozone column after the Carrington-Hodgson SPE for scenario E in comparison with the TOC without SPE impact for both the present day industrial atmosphere (upper figure) and the atmosphere of low halogen load (lower figure).

Figure 8.54: Antarctic total ozone column differences due to the Carrington-Hodgson SPE for scenario E for the present day industrial atmosphere in comparison with the atmosphere of low halogen load.
9. Long time series of solar proton events

In order to investigate the impacts of solar proton events on longer time periods, a modelled time series of SPE ionisations rates has been used. The series originates from stochastic simulations of solar particle events, a detailed description of the method is given by Steinhilber [2005]. In the following only the basic concept is briefly outlined. The nitrate deposits in ice cores from both Arctic and Antarctic and their relations with SPEs provide valuable information about the frequency of large and extremely large events within the last approximative 400 years [McCracken et al., 2001a+b]. But these proxy data lack information about smaller events and the lower energetic (<30 MeV) part of the large events. Therefore the nitrate proxy data alone cannot directly be used as a time series. But it is possible to obtain occurrence probabilities for major events from these data. In a sense complementarily, satellites have measured energy dependent particles fluxes since about three solar cycles including only a few really large events. From these measurements information about the energy spectra of SPEs of different sizes, and occurrence probabilities of smaller SPEs can be derived. Fortunately, there is an overlap between McCracken’s time series and the satellite data. In particular, the large SPEs in August 1972 and October 1989 are included in both data sets. While the latter was a sequence of SPEs which cannot unambiguously be related to the ice core event, the former as a single SPE could be used as a connector between the two data sets.

Based on the combined occurrence probabilities for SPEs, a time series of events has been generated. For each day a particle spectrum is randomly selected from the event size distribution whereas conditional probabilities are taken into account concerning the previous particles’ energy input to the atmosphere. Specifically, the occurrence probability for an event is correlated with the energy input a few days in advance and anti-correlated with the energy input about half a Schwabe cycle ago. The correlation with recent SPEs reproduces the typical short term solar activity patterns, and the longer term anti-correlation generates a quasi-cyclic behaviour resembling the Schwabe cycle. Longer activity periods, such as the Gleissberg cycle, are not accounted for. The resulting time series is not a historical one but as it is based on historical probability factors, it should represent a realistic situation.

The time period which has been used for this study is 200 years long. It covers more than 16 solar cycles and should be long enough to yield reliable mean values of ozone destruction. For such a long time period reasonably only the family model could be used. This model version does not provide results as accurate as the hybrid ion model but it should be sufficient to study the basic atmospheric responses for the different field configurations. The model atmosphere has been chosen to be an industrial atmosphere of year 2000. The geomagnetic field scenario F is not considered because from the simulations of the single SPEs it is not expected that this configuration would lead to results which significantly differ from the ones of other scenarios.
with large polar cusps, namely B and E. From the simulated time series of proton fluxes atmospheric ionisation rates have been calculated by the means of the Monte Carlo method. A 50 year section of the ion pair production rates in figure 9.1 shows the signature of several large events. In model year 119 there is an exceptional large SPE followed by another major event in year 120, see figure 9.2. Such a behaviour is not unrealistic. For instance, a period in the 1890s [McCracken et al., 2001a] suggests that at least three large SPEs each of which with fluences exceeding that of the August 1972 flare have occurred within only four years.

In the next section the modelled impacts on ozone are discussed, and afterwards the subsequent effects on the surface UV radiation and temperature are considered.

![Figure 9.1: Daily averaged ion pair production rates at 50 km height for the first fifty years of the simulated time series, courtesy of Friedhelm Steinhilber.](image1)

![Figure 9.2: Daily averaged ion pair production rates for the 200 year time series in linear scale at 84 and 42 km, respectively.](image2)

### 9.1 Chemical impacts

There are periods of high and low SPE activities in the simulated time series. Two characteristic sections of the 200 years have been selected to be looked at. The time period from model year 110 to 130 includes a very active SPE phase, and from year 130 to 150 there is a rather

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4Parts of the results presented in this section and in section 9.2 have been published in Winkler et al. [2007] (appendix B.1.)
quiet period (figure 9.2). For both intervals the NO\textsubscript{y} differences are shown in figure 9.3 and figure 9.4, respectively. Enhanced total NO\textsubscript{y} values are mainly located in the polar regions, and they are smallest for the equatorial dipole C. Qualitatively, all this agrees with the results of the previously discussed historical single SPEs, but the NO\textsubscript{y} production during the active phase around model year 120 is significantly larger. Accordingly, the ozone losses are larger than the ones which have been calculated for the single SPEs. The qualitative properties remain the same, though: In case of precipitating particles in the polar regions, the effect on ozone is much stronger than it is at lower latitudes. Figure 9.5 shows the modelled decrease of the total ozone column as a function of geographical latitude for the current magnetic field configuration A during the whole 200 years of the simulated SPE time series. As expected, the SPE caused ozone destructions are most pronounced in the polar regions, and although for that scenario the shielding by the Earth’s magnetic field is the same in both hemispheres the ozone losses in the southern polar region are significantly larger than the ones in the Arctic. Figure 9.5 also shows the TOC reduction during and several years after the intense SPE phase around model year 120 for the shielding scenario A. The total ozone losses for all other considered field configurations during the same time period can be seen in figure 9.6. The bulk of \(O_3\) loss is again found in the polar regions, strongest in the second half of model year 120 and at the beginning of year 121 in the southern polar region. This corresponds to the NO\textsubscript{y} abundances and again underlines the role of the atmospheric poleward transport and subsequent subsidence into the polar ozone layer. Also for scenario D the largest TOC reduction is found in both polar regions (figure 9.6). The patterns produced by D are quite similar to the ones of B. The configuration E with its large magnetic polar cusp being centred around the South pole experiences consequently the largest TOC reduction. It is the highest of all scenarios, exceeding 30% for more than one year. Figure 9.7 shows the 200 year mean ozone differences as a function of height and latitude. The large values in the upper mesosphere and above are not significant, they are an artefact of the family treatment. Besides that and the fact that they are more diluted, the geographical patterns of ozone losses look qualitative like the ones which have been calculated for one month after the Bastille event (on page 81).

A comparison of all scenarios’ mean TOC depletion as a function of latitude is shown in figure 9.8 and 9.9 for a time period of 200 years and 5.5 years, respectively. The latter corresponds to an interval of about half a solar cycle beginning in the middle of model year 119 and covers the most intense solar maximum period of the simulated SPE time series. The averaged ozone losses are largest in the southern polar region for all considered field scenarios. In all cases except for C, larger TOC differences at high latitudes are computed than for the current field configuration. For the magnetic field scenarios B, D, and E the ozone losses caused by large events reach values of ozone hole conditions, e.g. the peak ozone loss of E in the southern polar region exceeds 170 DU, its 5.5-year mean value is larger than 60 DU in comparison to about 20 DU for scenario A (again, the absolute values are too large, but their ratios are still meaningful). The 200 year average TOC losses are about as high as the maximum 12 month mean ozone reduction after the major SPE of 1859.

It has to be emphasised that these dramatic values arise from the high IPR rates of the simulated time series which are larger than what have been detected since several decades by the means of satellite observations. According to McCracken et al. [2001b], there have indeed been lower numbers of SPEs per Schwabe cycle in recent decades corresponding to a Gleissberg minimum. This contradicts the statement of Reedy [2002] that there has not been any reduced activity due to the Gleissberg cycle (already mentioned in section 2.1). The simulated time series with its high IPRs only provides a realistic picture if the SPE activity is nowadays lower than it had been on average in recent centuries. One should be aware of the fact that the CHE of 1859, which has
been derived from the nitrate proxy data as well, is significantly smaller than the major event in model year 119, though it is believed to be the largest historical SPE. In conclusion, the author would simply suggest to regard the time series as a possible accumulation of SPEs containing some exceptionally large events, without assessing its probability.

Figure 9.3: Total NO$_y$ column during model years 110–130 for the different geomagnetic field scenarios.
Figure 9.4: Total NO\textsubscript{y} column during model years 130–150 for the different geomagnetic field scenarios.
Figure 9.5: Modelled reduction of the total ozone column (TOC) in percentage for the present-day magnetic field configuration A. Left: 200 years of the simulated SPE time series. Right: 11 years during and after the intense SPE period starting at the end of model year 119.

Figure 9.6: Percentage decrease of the total ozone column (TOC) for the scenarios B to E during and several years after the intense SPE period starting at the end of model year 119 corresponding to figure 9.5 (right). In year 119 and at the beginning of year 120 the signals of two very large events can be seen in the tropics for case C, and D.
Figure 9.7: The 200 year mean ozone differences for all magnetic field scenarios.
9. Long time series of solar proton events

Figure 9.8: 200 year averages of SPE caused total ozone column (TOC) decrease in percentage versus geographical latitude for the scenarios A...E.

Figure 9.9: Like figure 9.8 but here are shown averages for a time period of 5.5 years during the very active SPE phase starting at the end of year 119 in the simulated time series.

9.2 Surface UV

The major effect of ozone losses on UV-B has already been mentioned and estimated in section 8.2.1. While there the UV changes have simply been calculated by scaling the TOC reduction with a constant radiative amplification factor, here a little bit more sophisticated method has been used:

Shorter wavelengths than UV-B are effectively absorbed by molecular oxygen and therefore the UV-C (100–280 nm) fluxes at sea level are quite small and not significantly affected by ozone changes. On the other hand, UV-C photons are rather potent in causing harmful effects, and thus this spectral range should not be ignored entirely. In the UV-A region (315–400 nm) the biological impacts are smaller but should also be taken into account. For some comments on more technical UV exposure criteria see Sliney [2000]. A suitable measure of the effective shortwave radiation exposure is the UV-Index

\[ I_{UV} = k \int_{\lambda_1}^{\lambda_2} E(\lambda) \cdot S(\lambda) \, d\lambda \]

where \( E(\lambda) \) denotes the spectral irradiance, and \( S(\lambda) \) is a dimensionless weighting function accounting for the wavelength dependent potency of the radiation. For different purposes respective weighting functions and intervals of integration can be used. To assess the UV impact on skin commonly the erythemal reference action spectrum by the International Commission on
Surface UV

Illumination [CIE, 1998] is used for $S(\lambda)$, and the integration interval is 250 nm to 400 nm. With $k = 40 \text{ Wm}^{-2}$, $I_{UV}$ becomes the dimensionless Solar UV Index recommended by the World Health Organization [WHO, 2002] for which the maximum $E(\lambda)$ around noon is used.

In order to estimate the impacts of the ozone losses on $I_{UV}$, the radiative transfer module SCIA-RAYS [Kaiser, 2001; Kaiser and Burrows, 2003] has been utilised. Originally, this program was developed to support retrievals of atmospheric parameters from limb scattering measurements by the SCIAMACHY instrument [Bovensmann et al., 1999] on-board the European environmental satellite ENVISAT. For the purpose of this study it is used to yield $E(\lambda)$ at ground level for clear sky conditions. The atmospheric model results in form of $O_3$ profiles, concentrations of several other trace gases, and temperature and pressure values are used as input data for SCIA-RAYS. The solar spectral irradiance applied on the top of the atmosphere is a measured daily-averaged spectrum (UARS SOLSTICE, [Rottman et al., 1993]) for February 2nd 1992.

The solar radiation reaching the Earth’s surface greatly depends on the solar zenith angle. In order to account for the different conditions in each season the radiative transfer simulations were performed for averaged atmospheric profiles of trace gases of the respective quarter year. In each case the lowest seasonal solar zenith angle at the particular latitude was applied to yield the maximum $I_{UV}$. Averaging the four seasonal values (shown in figure 9.10) roughly estimates an annual mean of $I_{UV}$ (the radiative transfer simulations are quite time-consuming, and the strict calculation of averages over several years would have caused unreasonable computing expenses).

As the TOCs are overestimated, the $I_{UV}$ values are too small, especially in the polar regions. Figure 9.11 shows the relative $I_{UV}$ changes for the different seasons. The calculated relative $I_{UV}$ increases correspond highly with the averaged relative TOC decreases, see figure 9.12. The radiation amplification factor lies between 0.95 and 1.2. The constant AF value of 1.1 which has been used in the previous sections to estimate the changes of the erythemal weighted UV-B radiation is indeed a good approximation, though in the polar regions the AF can be slightly smaller than 1. Figure 9.13 shows the relative $I_{UV}$ changes with respect to the present day field configuration represented by scenario A. While for the scenarios B, D, and E the $I_{UV}$ increases, especially at mid and high latitudes, for the equatorial dipole C the ultraviolet index almost everywhere decreases. Only in the tropics the latter scenario yields some slight $I_{UV}$ increase. The tropical $I_{UV}$ increase is largest for the axis-symmetric quadrupole field. The $I_{UV}$ increase at mid and low latitudes though smaller in terms of relative changes could be of importance as well because they add to already high $I_{UV}$ values.

Figure 9.10: Mean ultraviolet indices during the 5.5 very active years beginning at the end of model year 119.
Figure 9.11: Mean increases of the ultraviolet indices in the different seasons (DJF=December, January and February; MAM=March, April and May; ...) during the 5.5 very active years beginning at the end of model year 119 for the present day scenario A, left, and the dipole-quadrupole scenario E, right.

Figure 9.12: Mean increases of the ultraviolet indices during the 5.5 very active years beginning at the end of model year 119 in comparison with the corresponding total ozone losses for the present day scenario A, left, and the dipole-quadrupole scenario E, right.

Figure 9.13: Relative change of ultraviolet indices for the different scenarios with respect to the present day configuration of scenario A. Left: 200 year averages. Right: mean values for the 5.5 very active years beginning at the end of model year 119.
9.3 Atmospheric temperature

The 200 year mean values of temperature changes are depicted in figure 9.14 together with the average ozone losses. The atmospheric temperature tends to decrease. There are just some regions with slight warming, and the temperature increase nowhere exceeds +0.2 K. The decreasing temperatures in the lower polar stratosphere, especially in the South, denote a negative feedback on polar ozone as they facilitate the formation of polar stratospheric clouds and with that heterogeneous reactions which are important for ozone hole situations in spring times.

Figure 9.14: The 200 year mean temperature differences and the mean ozone losses as level lines for all magnetic field scenarios.
10. Summary and conclusions

Different geomagnetic field configurations, of which some are realistic representations for reversal situations, have been analysed with respect to their influence on atmospheric impacts of several single solar proton events. Additionally, enabled by a simulated 200 year time series of SPEs, impacts on longer time scales have been investigated. The simulations have shown that geomagnetic field variations can have considerable effects on the ozone destructions caused by solar proton events. In all magnetic shielding scenarios the ozone losses on longer time scales are most pronounced in the polar regions which indicates the importance of global transport of NO\textsubscript{y} and its subsidence into the ozone layer. The atmospheric impacts of single events depend significantly on the season in which they occur. On average, the ozone destruction is in general for all considered scenarios larger in the southern hemisphere than in the northern hemisphere. This is due to hemispheric differences in the transport processes.

In case of the present-day high halogen load in the stratosphere, there is an interference between halogen chemistry and SPE induced NO\textsubscript{y} perturbations especially during spring. This somewhat weakens the immediate SPE impact on ozone, but the general effect is that the anthropogenically burdened ozone layer is further negatively affected by large SPEs. The ozone losses are found to increase with the magnetic polar cusp size and with its nearness to the polar regions. In this sense, the current field configuration with its small tilt of geomagnetic to geographic axis is almost a worst case situation for the present field strength. The same cusp size in the tropics would cause much lower ozone destructions. The main reason for this is the strong photochemical destruction of NO\textsubscript{y} in combination with the basically nonexistent downward transport into the ozone layer at low latitudes. The very scenario of an equatorial dipole of actual cusp size can be regarded as a snap-shot of a hypothetical geomagnetic reversal with current field strength. As field reversals are very likely connected to field weakenings, they rather correspond to the other investigated scenarios which lead to significantly enhanced ozone depletions. For these geomagnetic field configurations, large events are able to cause considerable ozone losses, especially in the polar regions. With increasing cusp size also mid-latitudes become affected, but in general to a lesser extent than the polar regions. For all investigated single SPEs, the total ozone reductions are found to be smaller than due to an ozone hole. Nevertheless, especially in case of a large polar cusps, considerable ozone losses are found. In contrast to ozone holes, the impacts of SPEs on ozone are less restricted to spring times and early summer but can last for several years provided that the proton fluences are large. For exceptionally large SPEs, as they are included in the simulated time series, the total ozone losses can be comparable to ozone hole situations. Subsequently, harmful ultraviolet radiation increases at ground level.

The absolute ozone losses due to SPEs are smaller at mid-latitudes and in the tropics but due to smaller solar zenith angles the increasing erythemal weighted ultraviolet radiation might also be of importance in these regions. These results gain importance by the time scales of geomagnetic
field variations. For instance, in case of a full field reversal, for thousands of years the protecting ozone layer at high latitudes would be reduced to a notable extend, and consequently, UV fluxes would increase for the long time period of the reversal.

It has not been possible within the scope of this study to assess the possible biological impacts of these increased UV fluxes over time periods of thousands of years. However, it appears as if SPEs during field reversals are unlikely to directly cause (or have caused) mass-extinctions. On the other hand, major events in combination with a reduced shielding by the geomagnetic field have a negative effect on the surface UV burden which could impair living organisms, especially those how already suffer from other impacts.

The modelled temperature changes which arise from the SPE caused perturbations of the atmosphere’s chemistry are not very large. On average, the temperature tends to decrease in the middle atmosphere. According to the largest ozone losses, the cooling is strongest in the antarctic lower stratosphere. There the decreasing temperatures denote a negative feedback on ozone as they facilitate the formation of polar stratospheric clouds which provide surfaces for heterogeneous reactions which are important for ozone hole situations in spring times. In terms of global temperature change, the effect of SPEs seems to be of minor importance, even during a field reversal.
Appendix A

A.1 Reactions in the ion chemistry model

The rate coefficient are given in units of s⁻¹ for reactions involving one species, cm³ s⁻¹ for two body reactions, and cm⁶ s⁻¹ for three body reactions.

I) Cations and neutrals

<table>
<thead>
<tr>
<th>reaction</th>
<th>rate coefficient (reference/comment)</th>
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<tbody>
<tr>
<td>O⁺⁺(a²I) + N₂</td>
<td>N⁺⁺ + O₂</td>
</tr>
<tr>
<td>O⁺⁺(2D) + N₂</td>
<td>N⁺⁺ + O³P</td>
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<tr>
<td>O⁺⁺(2P) + N₂</td>
<td>N⁺⁺ + O³P</td>
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<tr>
<td>N⁺⁺ + O³P</td>
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<td>O⁺⁺⁺(S) + N₂</td>
</tr>
<tr>
<td>N⁺⁺ + NO</td>
<td>NO⁺ + N₂</td>
</tr>
<tr>
<td>N⁺⁺ + N⁺⁺(S)</td>
<td>N⁺⁺ + N₂</td>
</tr>
<tr>
<td>O⁺⁺⁺(S) + O₂</td>
<td>O⁺⁺ + O³P</td>
</tr>
<tr>
<td>O⁺⁺⁺(2D) + O₂</td>
<td>O⁺⁺ + O³P</td>
</tr>
<tr>
<td>N⁺ + O₂</td>
<td>O⁺⁺ + N⁺⁺(2D)</td>
</tr>
<tr>
<td>O⁺⁺⁺(a²I) + O</td>
<td>O⁺⁺ + O³P</td>
</tr>
<tr>
<td>O⁺⁺⁺ + N⁺⁺(2D)</td>
<td>N⁺⁺ + O₂</td>
</tr>
<tr>
<td>O⁺⁺⁺ + N⁺⁺(S)</td>
<td>NO⁺ + O³P</td>
</tr>
<tr>
<td>O⁺⁺ + NO</td>
<td>NO⁺ + N₂</td>
</tr>
<tr>
<td>O⁺⁺ + N₂</td>
<td>NO⁺ + NO</td>
</tr>
<tr>
<td>O⁺⁺(2D) + O³P</td>
<td>O⁺⁺⁺(S) + O³P</td>
</tr>
<tr>
<td>O⁺⁺(2D) + N₂</td>
<td>O⁺⁺⁺(S) + N₂</td>
</tr>
<tr>
<td>O⁺⁺⁺(2P) + O³P</td>
<td>O⁺⁺⁺(S) + O³P</td>
</tr>
<tr>
<td>O⁺⁺⁺(2P)</td>
<td>O⁺⁺⁺(S)</td>
</tr>
<tr>
<td>H⁺ + O³P</td>
<td>O⁺⁺⁺(S) + H⁺</td>
</tr>
<tr>
<td>N⁺ + O₂</td>
<td>O⁺⁺⁺(S) + NO</td>
</tr>
<tr>
<td>O⁺⁺⁺(S) + N₂</td>
<td>NO⁺ + N⁺⁺(S)</td>
</tr>
<tr>
<td>O⁺⁺⁺(S) + NO</td>
<td>NO⁺ + O³P</td>
</tr>
<tr>
<td>O⁺⁺⁺(S) + H₂</td>
<td>H⁺ + O³P</td>
</tr>
<tr>
<td>O⁺⁺⁺(S) + N⁺⁺(2D)</td>
<td>N⁺⁺ + O³P</td>
</tr>
<tr>
<td>O⁺⁺(2P)</td>
<td>O⁺⁺⁺(2D)</td>
</tr>
<tr>
<td>O⁺⁺(2D)</td>
<td>O⁺⁺⁺(S)</td>
</tr>
<tr>
<td>O⁺⁺(2P) + N₂</td>
<td>N⁺⁺ + NO</td>
</tr>
<tr>
<td>O⁺⁺⁺(a²I)</td>
<td>O⁺⁺⁺</td>
</tr>
<tr>
<td>O⁺⁺⁺(2P) + N⁺⁺(S)</td>
<td>N⁺⁺ + O³P</td>
</tr>
<tr>
<td>O⁺⁺(2D) + N⁺⁺(S)</td>
<td>N⁺⁺ + O³P</td>
</tr>
</tbody>
</table>
**Ib) Reactions involving acetonitril (CH₃CN=X)**

<table>
<thead>
<tr>
<th>reaction</th>
<th>rate coefficient (all from (6))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺(H₂O)₃ + X → H⁺(H₂O)₄(X) + H₂O</td>
<td>3.6 × 10⁻⁹</td>
</tr>
<tr>
<td>H⁺(H₂O)₂(X) + H₂O → H⁺(H₂O)₃ + X</td>
<td>3.5 × 10⁻¹⁶</td>
</tr>
<tr>
<td>H⁺(H₂O)₂(X) + H₂O + M → H⁺(H₂O)₃(X) + M</td>
<td>2.9 × 10⁻⁷ T⁻⁸.¹ = ♣</td>
</tr>
<tr>
<td>H⁺(H₂O)₃(X) + M → H⁺(H₂O)₂(X) + H₂O + M ♣/(8.4 × 10⁻²⁸ T exp(7252/T))</td>
<td></td>
</tr>
<tr>
<td>H⁺(H₂O)₄ + X → H⁺(H₂O)₃(X) + H₂O</td>
<td>3.3 × 10⁻⁹</td>
</tr>
<tr>
<td>H⁺(H₂O)₃(X) + H₂O → H⁺(H₂O)₄ + X</td>
<td>5 × 10⁻¹⁴</td>
</tr>
<tr>
<td>H⁺(H₂O)₃(X) + H₂O + M → H⁺(H₂O)₄(X) + M</td>
<td>1.52 × 10⁻¹⁴ =: ♣</td>
</tr>
<tr>
<td>H⁺(H₂O)₄(X) + M → H⁺(H₂O)₃(X) + H₂O + M ♣/(8.4 × 10⁻²⁸ T exp(5716/T))</td>
<td></td>
</tr>
<tr>
<td>H⁺(H₂O)₅ + X → H⁺(H₂O)₄(X) + H₂O</td>
<td>3 × 10⁻⁹</td>
</tr>
<tr>
<td>H⁺(H₂O)₄(X) + H₂O → H⁺(H₂O)₅ + H₂O</td>
<td>4.3 × 10⁻¹²</td>
</tr>
<tr>
<td>H⁺(H₂O)₄(X) + X → H⁺(H₂O)₃(X) + H₂O</td>
<td>7.2 × 10⁻¹⁰</td>
</tr>
<tr>
<td>H⁺(H₂O)₅(X) + + H₂O → H⁺(H₂O)₄(X) + H₂O</td>
<td>3.5 × 10⁻¹⁵</td>
</tr>
<tr>
<td>H⁺(H₂O)₄(X) + H₂O → H⁺(H₂O)₅(X) + X</td>
<td>2.9 × 10⁻⁷ T⁻⁸.¹ =: Δ</td>
</tr>
<tr>
<td>H⁺(H₂O)₅(X) + X → H⁺(H₂O)₄(X) + H₂O</td>
<td>9 × 10⁻¹⁴</td>
</tr>
<tr>
<td>H⁺(H₂O)₄(X) + H₂O + M → H⁺(H₂O)₅(X) + H₂O</td>
<td>4.3 × 10⁻¹²</td>
</tr>
<tr>
<td>H⁺(H₂O)₅(X) + + H₂O + M → H⁺(H₂O)₄(X) + + H₂O</td>
<td>4.3 × 10⁻¹²</td>
</tr>
</tbody>
</table>

**II) Anions and neutrals**

<table>
<thead>
<tr>
<th>reaction</th>
<th>rate coefficient (reference/comment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>e + O₂ + N₂ → X⁻ (+ N₂)</td>
<td>10⁻³¹</td>
</tr>
<tr>
<td>e + O₂ + O₂ → X⁻ (+ O₂)</td>
<td>4 × 10⁻³⁰ exp(-193/T)</td>
</tr>
<tr>
<td>e + O₃ → X⁻ (+ O₂)</td>
<td>9.1 × 10⁻¹² (T/300)⁰.⁴⁶</td>
</tr>
<tr>
<td>X⁻ + hv → e (+ X)</td>
<td>3.8 × 10⁻¹ cos(solar zenith angle)</td>
</tr>
</tbody>
</table>

**III) Anions with cations**

<table>
<thead>
<tr>
<th>reaction</th>
<th>rate coefficient (reference/comment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O⁺(³D) + e → O⁺(³S) + e</td>
<td>7.8 × 10⁻⁸ (T/300)⁻⁰.⁵</td>
</tr>
<tr>
<td>O⁺(³P) + e → O⁺(³S) + e</td>
<td>4 × 10⁻⁸ (T/300)⁻⁰.⁵</td>
</tr>
<tr>
<td>O⁺(³P) + e → O⁺(³D) + e</td>
<td>1.5 × 10⁻⁷ (T/300)⁻⁰.⁵</td>
</tr>
<tr>
<td>N⁺(³D) + e → N⁺(³S) + e</td>
<td>5.5 × 10⁻¹⁰ (T/300)⁻⁰.⁵</td>
</tr>
<tr>
<td>N₂ + e → N⁺(³D) + N⁺(³D)</td>
<td>1.8 × 10⁻⁷ (T/300)⁻⁰.³⁹ × 0.56</td>
</tr>
<tr>
<td>N₂ + e → N⁺(³S) + N⁺(³S)</td>
<td>1.8 × 10⁻⁷ (T/300)⁻⁰.³⁹ × 0.44</td>
</tr>
<tr>
<td>O⁺(³S) + e → O⁺(³P) + O⁺(³P)</td>
<td>1.8 × 10⁻⁷ (T/300)⁻⁰.³⁹ × 0.78</td>
</tr>
<tr>
<td>O⁺(³P) + e → O⁺(³P) + O⁺(³P)</td>
<td>1.8 × 10⁻⁷ (T/300)⁻⁰.³⁹ × 0.22</td>
</tr>
<tr>
<td>N⁺ + e → N⁺(³S)</td>
<td>1 × 10⁻¹²</td>
</tr>
<tr>
<td>O₂ + e → 2 O₂</td>
<td>4.2 × 10⁻⁶ (300/T)</td>
</tr>
<tr>
<td>O⁺(³S) + e → O⁺(³P)</td>
<td>4 × 10⁻¹² (300/T)⁰.⁷</td>
</tr>
</tbody>
</table>
A.2 The pre-ozone hole atmosphere

For all other cations’ recombinations with electrons:
\[ Y^+ + e \rightarrow \text{products} \quad 4 \times 10^{-6} \quad (5) \]

For all cations’ recombinations with \( X^- \):
\[ Y^+ + X^- \rightarrow \text{products} \quad 4 \times 10^{-6} \left( \frac{300}{T} \right) \quad (5) \]
\[ Y^+ + X^- + M \rightarrow \text{products} \quad 6 \times 10^{-26} (300/T)^4 \quad (5) \]

References and Comments:
1. Rees [1999].
2. Kazil [2002], not listed in Rees [1999].
3. Matsuoka et al. [1981].
4. As these reactions are included in the SLIMCAT scheme, they have been deactivated in the ion chemistry model.
5. Brasseur and Solomon [1986].
7. Reid et al. [1976].
8. Kazil [2002].
9. The amplitude value is for electron detachment from \( O_2^- \), for other species the values differ [Kazil, 2002]. The \( \cos(SZA) \) term was added to have at least a first order approximation for the changing rates with solar zenith angle.
10. Turunen et al. [1996].

A.2 The pre-ozone hole atmosphere

For the simulation (section 8.5) of an atmosphere prior to the increasing halogen concentrations during the industrial age, a pre-ozone hole atmosphere has been assembled. As all chlorofluorocarbons and halons are of industrial origin, they have been removed from the model atmosphere. There are some relevant halocarbons of anthropogenic as well as natural origin which are included in the SLIMCAT model. They have been treated as follows:

**Methyl Chloride (Chloromethane), CH\(_3\)Cl**, is the most abundant halocarbon in the atmosphere and is believed to be predominantly of natural origin. The analysis of atmospheric histories of halocarbons by the means of antarctic firn air by Trudinger et al., [2004] indicates a CH\(_3\)Cl mixing ratio for surface-near air of about 470 ppt at the beginning of the 20th century (in comparison to about 530 ppt in the year 2000) which approximately corresponds to other findings (e.g. Aydin et al., [2004]). As the Scientific Assessment of Ozone Depletion by the World Meteorological Organisation \([WMO, 2002]\) suggests a slightly lower value going further back in time, the CH\(_3\)Cl surface near mixing ratio has been chosen to be 450 ppt for pre-ozone hole conditions.

**Methyl Bromide (Bromomethane), CH\(_3\)Br**, is believed to have both anthropogenic as well as natural sources, and the division of its emission abundance into these two parts has been reason for scientific and regulatory controversy (Butler et al., [1999] and references therein). Motivated by the numbers given by Trudinger et al. [2004] and in WMO [2002], a surface near mixing ratio of 5 ppt has been guessimated for the pre-ozone hole atmosphere (in comparison to about 9.3 ppt in the year 2000).

**Carbon Tetrachloride, CCl\(_4\)**, is to a large extent of industrial origin but there are also natural sources. The contribution of the latter is difficult to assess. According to the rough estimates of WMO [2002], a surface near mixing ratio of 30 ppt has been chosen for pre-ozone hole (in
comparison to about 98 ppt in the year 2000).

**Methyl Chloroform, CH\textsubscript{3}CCl\textsubscript{3},** shows no significant abundance in polar firn air before its extensive industrial usage started [Butler et al., 1999], therefore it is set to zero for the pre-ozone hole conditions.
Appendix B

B.1 Publications related to the thesis

Publications in peer reviewed journals


Conference contributions


B.2 References

Agostinelli, S., et al. (tons of authors which are not omitted here because of ignorance but just because of practical reasons), GEANT4 - a simulation toolkit, NUCLEAR INSTRUMENTS AND METHODS IN PHYSICS RESEARCH A, 506, 250–303, DOI:10.1016/S0168-9002(03)01368-8 (2003)

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Royal II Royal Observatory of Belgium (data taken from http://www.astro.oma.be) on 12th February 2007


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Sun, Nitro, Gun (Sony BMG) (1996)


